

METHOD FOR INITIATOR-FREE SURFACE GRAFT COPOLYMERISATION WITH LAMINATION OF POLYMER FILMS IN ATMOSPHERE

BACKGROUND OF THE INVENTION



1. Field of the Invention

This invention relates to a method to impart adhesion or bonding between two contacting surfaces of similar or dissimilar polymers through the modification of the polymer surfaces by thermal or photo-induced grafting or graft polymerization. Under this method photografting or thermal grafting is induced with the polymer surfaces in contact, resulting in simultaneous lamination of the polymer substrates. Both the photografting and photolamination, or thermal grafting and thermal lamination are carried out under atmospheric condition in the complete absence of an added photoinitiator, thermal initiator or system degassing.

The properties can be imparted on the surface of most polymer films, including polyolefins, polyesters, hydrocarbon polymers, and fluoropolymers, as well as on the surface of electroattractive (conductive) and conjugated polymer. Photografting, thermal grafting or surface graft copolymerization with concurrent lamination can be carried out in the presence of one or more functional monomers including, but not limited to, acrylic acid (AAc), acrylamide (AAm), N,N-dimethylacrylamide (DMAA), N,N-dimethylpropylacrylamide (DMPAA), epoxide-containing monomers, hydroxy-containing monomers, amine-containing monomers, monomers of polyelectrolyte and monomers of polyampholyte.

The lap shear adhesion strength between two photolaminated or thermal laminated films can readily exceed the tensile yield strength of the substrate film. For example, shear adhesion strength in excess of 150 N/cm² can be readily achieved between two photolaminated surface. The thermal and photolamination strength arises from dispersive interaction, chain entanglement, electrostatic interaction. ionic



interaction, acid/base interaction. H-bonding, and/or covalent bonding between the grafted chains at the lapped junction. The present invention differs the prior art in that no added thermal initiator, photoinitiator and system degassing are required, and surface graft copolymerization and laminaion proceed under atmospheric conditions.

2. Description of the Related Art

In most engineering applications, a polymer is selected because of its favourable bulk properties, such as mechanical strength, electrical/electronic properties, thermal stability and processability. Often, however, the selected polymer has surface characteristics that are less than optimal for the intended application. This is particularly true in the case of adhesion involving inert polymer surfaces. To correct this shortcoming, various strategies of surface chemical modification have been implemented. They have been described, for example, in S. Wu, *Polymer Interfaces and Adhesion*, Marcel Dekker, N. Y. (1982); Y. Ikada and Y. Uyama, *Lubrication Polymer Surfaces*, Technomics Pub. Co. Inc., Lancaster, PA (1993); K. L. Mittal, (Ed.) *Polymer Surface Modification: Relevance to Adhesion*, VSP, Zeist, The Netherlands (1995); L. S. Penn and H. Wang, *Polymers for Advanced Technologies*, 5, 809-817 (1994); and E. T. Kang, K. G. Neoh, K. L. Tan, F. C. Loh and D. J. Liaw, *Polymers for Advanced Technologies*, 5, 837-842 (1994).

A variety of techniques are useful for chemical modification of polymer surfaces for improved adhesion. These techniques include acid etching, X-ray exposure, γ -ray irradiation, ultraviolet irradiation, electron beam bombardment, ozone treatment, corona discharge treatment, and plasma treatment. The last technique has been described, for example, in M. Strobel, C. S. Lyons and K. L. Mittal (Ed.) *Plasma Surface Modification of Polymers: Relevance to Adhesion*, VSP, Zeist, The Netherlands (1994). A variety of polar and functional groups are generated on the polymer surface, as a result of these treatments. One of the major drawbacks of these treatments is that the physicochemical characteristics of the modified polymer surface, 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, as the polar and functional groups generated on the polymer surfaces by these methods are generally of micromolecular in nature and are generally restricted to a few surface molecular layers, adhesion between two modified polymer surfaces is promoted only in the presence of an externally applied adhesive. As an alternative to the generation of micromolecular functional groups at the surface, macromolecules with repeating functional units can be incorporated at the surface through, for example, surface graft copolymerization. Thus, surface graft copolymerization allows specific functional groups to be introduced, in principle, onto all polymer surfaces in substantially enhanced quantity and spatial versatility. The presence of simultaneous interactions among the growing chains from the two contacting film surfaces during grafting or graft copolymerization will readily result in strong adhesion between the two surfaces in the absence of an added adhesive.

Recently, an innovative bulk surface photografting process, in which a drop of solution containing a monomer and a photoinitiator was sandwiched between two thin films, had been reported in W. T. Yang and R. Ranby, *Macromolecules*, 29, 3308-3310 (1996), W. T. Yang and R. Ranby *J. Appl. Polym. Sci.*, 62, 533-543 (1996), W. T. Yang and R. Ranby, *J. Appl. Polym. Sci.*, 62, 545-555 (1996), and W. T. Yang, *Lamination by Photografting, PhD Thesis*, Department of Polymer Technology, Royal Institute of Technology, 10044 Stockholm, Sweden (1996). Most importantly, photolamination occurred simultaneously during the photografting process, resulting in strong adhesion between the two films. A number of studies had also reported on the successful incorporation of functional groups onto polymer surfaces via graft copolymerization in the absence of an added photoinitiator but in the presence of system degassing. However no simultaneous photolamination phenomenon was reported or explored. These studies include those of E. Uchida, Y. Uyama and Y. Ikada, *J. Polym. Sci., Part A : Polym. Chem.*, 27, 527-538 (1989); M. Mori, Y. Uyama and Y. Ikada, *J. Polym. Sci., Part A: Polym. Chem.*, 32, 1603-1690 (1994); E. T. Kang, K. L. Tan, K. Kato, Y. Uyama and Y. Ikada, *Macromolecules*, 29, 6872-6879 (1996); and X. Zhang, E. T. Kang, K. G. Neoh, K. L. Tan, D. Y. Kim and C. Y. Kim, *J. Appl. Polym. Sci.*, 68, 625-636 (1996).

The patent literature contains a multitude of references to surface modifications of polymers for adhesion enhancement. Relatively few, however, are directly related to surface modification via graft copolymerization for adhesion improvement. A specific patent search for the simultaneous photografting and photolamination in the absence of an added photoinitiator and system degassing did not reveal any similar published prior art. Some prior art of interest is summarised below.

US Patent No. 4,968,532, dated November 6, 1990, discloses a process for modifying the surface characteristics of a pre-formed polymeric substrate to impart hydrophilicity, hydrophobicity, or other properties. The process comprises peroxidizing and hydroperoxidizing the surface of said substrate using ozone, followed by exposing the substrate in an inert gas-purged (degassed) monomer solution to affect thermal graft copolymerization at the substrate surface.

US Patent No. 4,589, 964, dated May 20, 1986, discloses a process for modifying the surface characteristics of a pre-formed polymeric substrate to impart hydrophilicity, hydrophobicity, or other desired properties there to, by peroxidizing the surface of the substrate, followed by graft copolymerization in the presence of variable valence metal ions in a reduced state under acidic conditions.

US Patent No. Re. 32,217, dated July 29, 1986, relates to mass graft copolymerization carried out in an extrusion passageway having a sealing zone to prevent back flow of grafting material introduced to the extrusion passageway downstream of the sealing zone.

US Patent No. 4,526,579, dated January 20, 1986, discloses a process for graft copolymerization of certain alpha-vinyl carboxylic acid anhydride monomers onto the surface of a natural rubber article and subsequent hydrolysis of anhydride to form hydrophilic carboxylate groups.

Japanese Patent JP7,101,017A, dated April 18, 1995, discloses how an easy adhesive resin layer is prepared to make a polyester film useful for a magnetic recording medium.

Japanese Patent JP7, 216,319A, dated August 15, 1995, discloses a self-adhesive sheet, having an adhesive layer composed of elastomer, tackifier resin, softener and incompatible macromolecular compound.

German Patent DE 4, 410,558A1, dated September 28, 1995, discloses the preparation of a malleable, multi-layered, self-adhesive screening sheet or strip to carry conductors; and pipes which screens electromagnetic field and radiation for use as a conduit system.

Japanese Patent JP7,216,322A, dated August 15, 1995, relates to the production of a self-adhesive non-vulcanized rubber sheet or tap by laminating a self-adhesive non-vulcanized rubber on a surface material, the surface material is temporarily bonded to a release paper and the a self-adhesive rubber is laminated on it, followed by winding the laminate into a roll.

Japanese Patent JP 7,216,315A, dated August 15, 1995, discloses the preparation of a self-adhesive film leaving no residue on the substrate, prepared by forming a thin metal layer on supporting film made from, for example, polyolefin and self-adhesive layer on other side of the supporting film.

Japanese Patent JP 7,188,634A, dated July 25, 1995, relates to a one pack curable epoxy resin self-adhesive for self-adhesive tape , comprising of epoxy resin, ketimine, modified silicone resin catalyst for modified silicone resin, and tack improver.

In International Patent WO 9,411,421, dated May 26,1994; and European Patent EP 667,879, dated August 23, 1995, modification of polymer-based surfaces by coating with particles is affected without the use of an adhesive by converting the surface top layer to a swollen or semi-dissolved state and simultaneously or subsequently contacting it with the particles.

In European Patent EP 358,519A, dated March 24, 1990; Japanese Patent JP 2,073,828A, dated March 13, 1990; Japanese Patent JP 2,245,033A, dated September 28, 1990; US Patent No. 5,049,626, dated September 17, 1991; European Patent EP 358,519A3, dated March 18, 1992; and US Patent No. 5,300,548, dated April 5, 1994, a graft copolymer comprises a stock copolymer of monomers from esters of unsaturated carboxylic acids and vinyl esters, ethylene, and CO, and a polyamide oligomer having a primary amino group at one end of its molecule grafted on the stock has been disclosed.

In Japanese Patent JP 4,370,107A, dated December 22, 1992, a modified copolyester is obtained by polymerising an unsaturated monomer bearing no hydrophilic groups in medium in presence of a copolyester bearing no substituents of sulfonic acid derivatives. Also disclosed are easily adhesive polyester films obtained by applying aqueous solution of the modified copolyester on at least one side of a polyester film.

According to German Patent DE 3,602,800A, dated December 11, 1986; European Patent, EP 204,943A, dated December 17, 1986; US Patent No. 4,740,562, dated April 26, 1988; and German Patent DE 3,602,800C, the surface of polyvinylidene fluoride articles is modified by de-hydrofluorination, by etching with base, solvent or swelling agent and homogenising agent, to improve adhesion and hydrophilicity.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for imparting adhesion between two contacting polymer surfaces through simultaneous photografting and photolamination, or through simultaneous thermal grafting and thermal lamination under atmospheric conditions.

It is also an object of the present invention to provide a process for the simultaneous photografting and photolamination, or thermal grafting and thermal lamination, in the complete absence of an added photoinitiator or thermal initiator, and without prior degassing of the system.

The objects of the present invention can be imparted on all polymer film pairs, including film pairs and combinations of polyolefin, polyester, hydrocarbon polymers, fluoropolymers, electroactive (conductive) and conjugated polymers, as well as thermoset polymers.

In the case of simultaneous photografting and photolamination, the preferred application and the best advantages of the present invention are obtained from polymer film pair, in which one of the films is transparent or semi-transparent to UV or near-UV light.

Another advantage of the present invention is that the thermal and photolamination are not limited to two similar or identical polymer substrates, but are also obtained between polymer films with vastly different physicochemical properties and compositions, such as between a fluoropolymer film and a polyolefin film.

These and other objects and advantages of the present invention are obtained according to a first aspect of the invention by providing a method for activating the surfaces of two contacting polymers such as two polymer films. The preferred method is ozone treatment, inert gas plasma treatment, or treatment by corona discharge.

The objects and advantages of the present invention are realised when two surface preactivated polymers, such as two surface preactivated polymer films are brought into intimate contact with each other in the presence of a small amount of a functional vinyl monomer. The interfacial adhesion strength is fully developed when the assembly is exposed to UV light or to elevated temperature to effect graft copolymerization at the interface.

The objects and advantages of the present invention are fully achieved when the grafted polymer chains from the two lapped films undergo diffusion and entanglement, inductive and dispersive interactions, ionic and electrostatic interaction, H-bonding, covalent bonding, and/or crosslinking at the interface.

The monomers for graft copolymerization and lamination are selected from a family of vinyl monomers which readily undergo free-radical initiated polymerization. Desirably, the monomers are selected from the group containing polar, cationic, anionic, amphoteric or electrolyte functional moieties.

More particularly, said functional monomers are selected from the family of liquid vinyl monomers. The monomers used thereof may be selected from the families of acrylic acid-based monomers, acrylamide and acrylate monomers, glycidyl or epoxy-containing monomers, amine-containing monomers, and families of vinylimidazole monomers.

The functional monomers are also selected from the family of solid vinyl monomers which are soluble in water or common organic solvent. For effective thermal or UV induced graft copolymerization and lamination in the absence of an added initiator and without prior system degassing, a solution containing 20wt.% and above of the monomer is preferred. The solid monomers thereof may be selected from acrylamide and acrylate monomers, sulfonic acid-containing monomers, monomers of polyelectrolytes, and amphoteric monomers.

The substrate polymer films used thereof may be selected from polyolefins and hydrocarbon polymers, such as, but not limited to, high density polyethylene, low density polyethylene, polystyrene, polypropylene and polycarbonate etc.; polyester films, such as, but not limited to, poly (ethylene terephthalate) etc.; fluoropolymers, such as, but not limited to, polytetrafluoroethylene, poly (vinylidene fluoride), and their copolymers. Thermoset films or polymer films with thermoset characters, such as, but not limited to, epoxy and polyimide films etc. may also be selected. Conjugated or electroactive polymer films, such as, but not limited to, films of aniline, pyrrole,

thiophene, substituted acetylene, and phenylene vinylene polymers, and their derivatives and analogs, may also be used as substrates.

The objects and advantages of the present invention are substantially enhanced if the grafted polymer chains at the laminated interface also exhibit ionic bonding, polar interaction, H-bonding, and/or bonding through metal chelation.

The objects and advantages of the present invention are also significantly enhanced if the grafted polymer chains at the lapped interface undergo covalent bonding and crosslinking. More particularly, when the substrate surfaces of the lapped junction are graft copolymerized with curable monomers, such as, but not limited to, epoxide, unsaturated ester, urethane, silicone and phenol-based monomers and their respective curing agent. The curing reactions during lamination readily result in a covalently bonded and crosslinked interface with high adhesion strength.

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 the introduction of functional polymers, through radical initiated, surface graft copolymerization at the lapped junction between two polymer films, readily results in the simultaneous lamination of the two polymer surfaces. The present invention differs from the prior arts in that no polymerization initiator or system degassing are needed and the graft copolymerization and lamination are carried out under atmospheric conditions. Thus, the surface of a preactivated thin film or substrate is capable of undergoing thermal or near-UV induced graft copolymerization when coated with a thin layer of functional monomer or monomer solution and covered with an inert substrate. The inert substrate should be semi-transparent or transparent to the near-UV light in the case of photo-induced graft copolymerization. Simultaneous graft copolymerization and lamination occur when the other substrate is another preactivated polymer film (not necessary of the same material and composition). The adhesion or lamination strength, is governed by the nature of the interaction between the graft chains at the lapped junction. The

interfacial interactions arise from inductive, dispersive (van der Waals), ionic, electrostatic covalent bonding, and H-bonding forces. In all cases, chain diffusion and entanglement at the lapped junction play an important role in the resulting adhesion strength. The type of interfacial interaction is determined, in term, by the type of functional groups in the surface grafted polymer. The extent of entanglement, on the other hand, depends on the efficiency and density of surface grafting.

It is well-known in the scientific literature that a number of vinyl monomers are susceptible to near-UV-light or thermal induced radical polymerization. The monomers used in the present invention are chosen from this family of vinyl monomers. The graft copolymerization reactions are initiated by free radicals generated on the substrate surface. Thus, prior to graft copolymerization, the substrate films are pretreated with plasma, ozone, corona discharge or other chemical and physical means to produce a surface coverage of peroxides and hydroxyl peroxides. The peroxide species on the surfaces of two contacting films are subsequently decomposed thermally or by near-UV-light to initiate the surface graft copolymerization reaction and simultaneous lamination in the presence of the monomer or monomers.

The selection of the type of surface activation for the substrate films prior to surface graft copolymerization and lamination is of particular importance. For chemically inert surfaces, such as the surfaces of most fluoropolymers films, the choices of surface pretreatment are limited to plasma and corona discharge treatments. For the polyolefin, polyester, polyimide, polycarbonate and hydrocarbon films, the choice of the surface activation methods is less restricted. Due to the reactive nature of the conjugated electroactive polymer surfaces, graft copolymerization can proceed in the absence of any surface pretreatment.

The selection of the monomer concentrations used for graft copolymerization in the absence of initiator and system degassing is of great importance. For liquid monomers, pure monomer is preferred, although reaction will proceed with solution containing as little as 10% monomer by weight. For solid monomers, a monomer concentration above 20wt% is preferred, although a 10wt.% monomer solution can

also be used. For lower monomer concentration used, a longer time is needed to initiate the reaction and, in some cases, to reach the same extent of surface grafting. The best adhesion results are obtained (i) when both chain entanglement and electrostatic interactions co-exist, and (ii) when covalent bonding or crosslinking exist among the grafted chains between the two lapped surfaces. With the presence of sufficient chain diffusion and entanglement, electrostatic and/or covalent bonding at the lapped junction, simultaneous lamination can be observed between two similar or between two dissimilar substrate films. It should be noted, however, that polymer films of different chemical structure and composition will exhibit different susceptibility towards graft copolymerization with the select monomer under the same experimental conditions.

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 examples 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. For all systems studied: (i) no polymerization initiator was added in the monomers or monomer solution, (ii) no system degassing or purging with inert gas was carried out, and (iii) all reactions were carried under atmospheric conditions. Example 1 provides more details on the conduct of the experimental process of surface graft copolymerization with concurrent lamination.

While the examples have been carried to show that the method works under atmospheric conditions without the need for degassing or inert atmospheres it should be obvious that the method will work under vacuum or inert atmospheres, if desired for example, in applications relating to packaging of electronic circuits or devices.

EXAMPLE 1

In a preferred experimental scale process, two Ar plasma pretreated, ozone pretreated, or corona discharge pretreated low density polyethylene (LDPE) films of size 0.5cm × 2 cm were lapped together with a contact area of 0.5 cm × 0.2 cm in the presence of a small amount of pure AAc monomer. The LDPE/AAc/LDPE assembly was then subjected to near-UV-light illumination for 2 to 20 min with a 150 W Xenon arc source. Alternatively, the film assembly was placed in a constant temperature oven for 0.5 to 3h. The temperature of the oven was chosen between 60 to 90°C. After the near-UV-light or high temperature treatment, the lapped films were subject to lap shear adhesion test. For the LDPE/AAc/LDPE assembly, the lap shear adhesion strengths resulting from the photolamination and the thermal lamination processes were about 110 and 100 N/cm², respectively.

EXAMPLE 2

In a preferred thermal graft copolymerization with concurrent lamination experiment, two Ar plasma-pretreated polytetrafluoroethylene (PTFE) films of 0.5 cm × 2 cm in size were lapped together with a contact area of 0.5cm × 0.1cm and in the presence of a small quantity of the aqueous solution containing 50 wt.% or less of DMAPS amphoteric monomer. The PTFE/DMAPS-H₂O/PTFE assembly was placed in a constant temperature oven for 0.5 to 3 h. The temperature of the oven was chosen between 60 to 90°C. Lap shear adhesion strength resulting from this simultaneous thermal grafting and thermal lamination process readily exceeds 90 N/cm².

EXAMPLE 3

In a preferred photolamination experiment, an ozone-pretreated LDPE film and an ozone-pretreated poly(ethylene terephthalate) (PET) film of 0.5cm × 2cm in size were lapped together with a contact area of 0.5cm×0.2cm and in the presence of a small quantity of pure AAc monomer. The LDPE/AAc/PET assembly exhibited a lap shear adhesion strength of about 100 N/cm² when illuminated by a 150 W Xenon source for 10 min from the LDPE side.

EXAMPLE 4

In another preferred photografting and photolamination experiment, Ar plasma pretreated PTFE and LDPE films of 0.5cm × 2cm in size were lapped together with a contact area of 0.1cm × 0.5cm in the presence of a small quantity of 50 wt.% or less of aqueous AAc monomer solution. The PTFE/AAc/LDPE assembly exhibited a lap shear adhesion strength of about 70 N/cm² when illuminated by a 150 W Xenon source for 20 min from the LDPE side.

EXAMPLE 5

In another preferred thermal graft copolymerization and thermal lamination experiment, two Ar plasma pretreated PTFE films of 0.5cm × 2cm in size was lapped together with a contact area of 0.1cm × 0.5cm in the presence of a small quantity of glycidyl methacrylate(GMA) - 2-hydroxyethyl methacrylate(HEMA) mixture. The PTFE/GMA-HEMA/PTFE assembly was subjected to thermal treatment at 90°C for 3h. In this case, the thermally grafted GMA and HEMA polymers also underwent covalent bonding and crosslinking in the lapped junction, resulting in strong lamination between the two PTFE film. The lap shear adhesion strength of the thermally cured assembly readily exceeded the tensile yield strength of the PTFE film even only with the small lapped area.

EXAMPLE 6

In yet another preferred simultaneous thermal graft copolymerization and thermal lamination experiment, a Ar plasma-pretreated PTFE film and a pristine emeraldine (EM) base film of polyaniline of 0.5cm × 2cm in size were lapped together with a contact area of 0.1cm × 0.5cm in the presence of a small quantity of aqueous solution containing 50 wt.% or less of DMAPS. The PTFE/DMAPS-H₂O/EM assembly exhibits a lap shear adhesion strength in excess of 100 N/cm² after exposure to a temperature of 90°C in a constant temperature oven for about 2 h.

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 disclosure and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

CLAIMS

1. A method to impart adhesion between two contacting polymer surfaces through simultaneous photografting and lamination in the presence of a monomer or mixture of monomers but in the absence of initiators and without degassing, comprising the steps of:
 - a. pretreating the polymer contacting surfaces with a rare gas plasma, corona discharge, ozone, gamma ray or laser,
 - b. lapping the said pretreated polymer surfaces in contact with a small amount of a functional monomer or mixture of monomers,
 - c. irradiating with ultra-violet light the contacting surfaces and concurrently maintaining the said surfaces in contact until simultaneous surface graft copolymerization and lamination occur.
2. A method to impart adhesion between two contacting polymer surfaces through simultaneous thermal grafting and lamination in the presence of a monomer or mixture of monomers but in the absence of initiators and without degassing, comprising the steps of:
 - a. pretreating the polymer contacting surfaces with rare gas plasma, corona discharge, ozone, gamma ray or laser,
 - b. lapping the pretreated polymer surfaces in contact with a small amount of a functional monomer or mixture of monomers,
 - c. subjecting the said lapped polymer surfaces to thermal treatment at elevated temperatures below the glass transition temperature of the polymer(s) and concurrently maintaining the said surfaces in contact until simultaneous surface graft copolymerization and lamination occur.

3. The method according to claim 1 or claim 2, wherein one or both of the two contacting polymer surfaces are similar or dissimilar polymer films and wherein at least one of the said polymer films allows the transmission of ultra-violet light.
4. The method according to any one of the preceding claims, wherein any one or both of the polymers are selected from the families of polyolefin and hydrocarbon polymers such as high density polyethylene, low density polyethylene, polypropylene, polystyrene, polycarbonate, and their derivatives and analogs.
5. The method according to any one of claims 1 to 3, wherein any one or both of the polymers are selected from the family of fluoropolymers, consisting of polytetrafluoroethylene and its derivatives and copolymers, including copolymers of tetrafluoroethylene and hexafluoropropylene, copolymers of tetrafluoroethylene and perfluoro (propyl vinyl ether), copolymers of tetrafluoroethylene and vinyl chloride, copolymers of tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxide, poly(vinyl fluoride), poly (vinylidene fluoride), polychlorotrifluoroethylene, vinyl fluoride/vinylidene fluoride copolymers, and vinylidene fluoride/hexafluoroethylene copolymers.
6. The method according to any one of claims 1 to 3, wherein any one or both of the polymers may also be selected from the family of polyesters, including poly (ethylene terephthalate).
7. The method according to any one of claims 1 to 3, wherein any one or both of the polymers may also be selected from the family of thermosetters, including epoxy polymers, polyimides, polyurethanes, and phenolic polymers.
8. The method according to any one of claims 1 to 3, wherein any one or both of the polymers may also be selected from other halogen-containing polymers including poly (vinyl chloride) and poly (vinylidene chloride).

9. The method according to claim 1 or claim 2, wherein the monomer for the simultaneous surface graft copolymerization and lamination are selected from the group of hydrophilic vinyl monomers, including the acrylic acid-based monomers, acrylamide monomers, sulfonic acid-containing monomers, and acrylate monomers, such as 2-hydroxy-ethylmethacrylate (HEMA).
10. The method according to claim 4 or claim 5 wherein said polymers are also selected from other halogen-containing polymers, including poly (vinyl chloride) and poly (vinylidene chloride).
11. The method according to claim 4 or claim 5 wherein said polymers are also selected from the family of electroactive conjugated polymers, including the aniline, pyrrole, thiophene, acetylene polymers and their derivatives and analogs.
12. The method according to claim 1 or claim 2 wherein the monomer for the simultaneous surface graft copolymerization and lamination are also selected from the group of electrolyte, Zwitterionic, and amphoteric monomers, including dimethyl sulfate quaternized dimethylaminoethylmethacrylate (DMAEM.C₂H₅SO₄), 3-dimethyl (acryloyloxyethyl) ammonium propanesulfonate (DAAPS), 2-acrylamino-2-methylpropanesulfonate, and 3-dimethyl (methacryloyl ethyl) ammonium propanesulfonate (DMAPS).
13. The method according to claim 1 or claim 2 wherein the monomers for the simultaneous surface graft copolymerization and lamination are also selected from the group of epoxide-containing monomers, including glycidyl methacrylate, ally glycidyl ether, and glycidyl functional aromatic monomers.

14. The method according to claim 1 or claim 2 wherein the monomers for the simultaneous surface graft copolymerization and lamination are also selected from the group containing epoxy curing functionalities, including N-(hydroxymethyl) acrylamide, and N-(butoxymethyl) acrylamide.
15. The method according to claim 1 or claim 2 wherein two or more different monomers with functional groups which are capable of covalent bond formation are used for the simultaneous surface graft copolymerization and lamination.