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METHOD TO PROMOTE GROWTH AND ADHESION OF ELECTROACTIVE POLYMER COATINGS ON CONVENTIONAL POLYMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for enhancing the growth and adhesion of electrically conductive polymer coatings on a substrate. The process calls for the modification of the substrate's surface via graft copolymerization with hydrophilic monomers and contacting the modified surface with a reaction mixture of monomer, oxidizing agent and doping agent or counterion.

2. Description of Related Art

The potential applications of electroactive polymers are limited by the problems of processibility, cost and strength. The electroactive polymers, polypyrrole and polyaniline, which have high conductivity and are fairly easy to synthesize are soluble only in a very limited number of solvents. The films of these polymers, either synthesized electrochemically or cast from solution, lack mechanical strength. Thus, these problems and the problem of cost of using "pure" electroactive films have caused investigators to pay increasing attention to electroactive coatings on conventional polymeric substrates.

There are various methods of depositing an electroactive film on a non-conducting substrate. One method involves the synthesis of the electroactive polymer, dissolution of the polymer in an appropriate solvent and exposing the substrate to the solution. However, as-synthesized polyaniline and polypyrrole salts show limited solubility.

Various methods have been employed to improve the solubility of polyaniline and polypyrrole salts to facilitate postsynthetic processing, eg. (i) introduction of sulfonic acid groups into the polymer backbone via treatment with fuming sulfuric acid (J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid, *J. Am. Chem. Soc.*, 113, 2665-2671 (1991)) (ii) use of ring substituted aniline or pyrrole monomers (K.G. Neoh, E.T. Kang and K.L. Tan, *Synth. Met.* 60, 13-21 (1993)); M.T. Nguyen and A.F. Diaz, *Macromolecules* 28 (3411-3445) 1994; H. Masuda, S. Tanaka and K. Kaeriyama, *Synth. Met.* 33, 365-372 (1989)) and (iii) counterion induced processibility by the use of suitably functionalized protonic acids (Y. Cao, P. Smith and A.J. Heeger, *Synth. Met.* 48, 91-97 (1992); J.Y. Lee, D.Y. Kim and C.Y. Kim, *Synth. Met.* 74, 103-106 (1995)).

Alternatively, the polyaniline salt can be undoped to the base form which is suitable for film casting using N-methylpyrrolidinone (M. Angelopoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, M. Akhtar, F. Kiss and A.J. Epstein, *Mol. Cryst. Liq. Cryst.* 160, 151-163 (1988)). However, such base films are insulating and must undergo subsequent redoping with a protonic acid to be conductive.

All the above mentioned methods suffer a major drawback of being a two-step process, a polymerization step followed by the coating step. N.M. Ratcliffe reported in US Patent 5,089,294 a simple procedure of preparing conductive films by dipping a non-conducting substrate in, or otherwise contacting the substrate with, a colloidal suspension of polypyrrole which is prepared from an oxidizing agent and pyrrole. A simultaneous polymerization and coating process utilizing polypyrrole as a coating material on fibers to prepare conductive fabrics has been described by H.H. Kuhn in US Patent 5,108,829. An alternative method of forming a conductive coating by imbibing an aqueous aniline solution on an organic film or fiber and polymerizing the aniline in-situ by contacting the fiber or film with an oxidizing catalyst in an aqueous acid medium has also been reported by C.H. Hsu and E. Vance in European Application 0355-518 A2. A method of forming

conductive polymer film on substrates pretreated with initiators is described by C.C. Han et. al. in US Patent 5,225,495. In that method, the substrate is first contacted with an initiating agent. In the second step, the pretreated substrate is contacted with a solution of the conjugated monomer and an oxidizing agent having an oxidation potential greater than that of the initiating agent. It is a requirement that the initiating agent have an oxidation potential less than that of the monomer and is capable when oxidized of reacting with and coupling to the monomer to initiate polymerization of the monomer. This method is reported to result in strongly adherent conductive polymer coating because of the covalent bonds between the conducting polymer and initiator.

Other US Patents relating to the subject are summarized below :

US Patent 4,937,060 discloses an inorganic powdery or granular material is coated with a coating of an inherently conductive polymeric material, such as polypyrrole, polythiophene, polyaniline and their substituted analogs.

US Patent 5,266,617, relates to a Lewis base catalyzed phase transfer coating process for coating a substrate with an acid substituted polyaniline.

US Patent 5,494,609 discloses a method for the preparation of electrically conductive coating compositions which includes the steps of preparing a dispersion of an intrinsically conductive polymer in a film forming thermoplastic matrix and the steps of dissolving the dispersion in an organic solvent and forming a film from the dissolved dispersion has been claimed.

US Patent 5,618,469 provides a solution comprising a proton-doped polyaniline in combination with a protonic acid which is a solvent thereof, and an article coated with an optically transparent, electrically conductive layer formed from the solution.

SUMMARY OF THE INVENTION

The present invention relates to a method of enhancing the growth and adhesion of an electrically conductive polymer coating on a substrate which has been functionalized via graft copolymerization with hydrophilic monomers. The preferred substrates and the best advantages of the present invention are obtained with polymeric substrates. The polymeric substrates used thereof may be selected from but are not limited to polyolefins, polyesters, polycarbonates etc. The objects and advantages of the present invention are obtained by providing first a method for modifying the surfaces of the substrate. The preferred method of surface modification is via thermally or near-UV-light induced surface graft copolymerization of the pre-activated substrate surfaces with functional monomers. The monomers for the surface graft copolymerization are selected from a family of vinyl monomers which readily undergo free-radical initiated polymerization. More particularly, the said functional monomers are selected from the family of water-soluble or hydrophilic monomers such as but not limited to the acrylic acid-based monomers, acrylamide and acrylate monomers and sulfonic acid-containing monomers. This allows the objects and advantages of the present invention to be achieved using water as the solvent medium.

The coating of the electrically conductive polymer on the surface modified substrate is carried out by contacting the said substrate with a reaction mixture of the conjugated monomer, oxidizing agent and doping agent or counterion. The preferred application and the best advantages of the present invention are obtained when the conjugated monomers are aniline or pyrrole monomers, their derivatives and analogs and the polymerization is carried out in an aqueous medium. The objects and advantages of the present invention are achieved when the conjugated polymer chains undergo entanglement and electrostatic interactions with the graft copolymer chains on the substrate's surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the first step of the process of this invention, a substrate is subjected to pretreatment to produce a surface coverage of peroxide and hydroxyl peroxide species. Methods to generate these species include treatment with plasma, ozone and corona discharge. The peroxide species are subsequently decomposed thermally or by near-UV light to initiate surface graft copolymerization reactions in the presence of the monomer. The substrates which can be used in this invention may vary widely. The only requirement is that the surface of the substrate can be treated to generate the species which can initiate the graft copolymerization reactions. The choice of surface pretreatment method will be dependent on the substrate. The monomers for graft copolymerization used in this invention are vinyl monomers which contain either polar, cationic or anionic functional groups. The selection of the monomer concentration is not particularly important, although the preferred concentration is 10 wt%. For lower monomer concentration used, a longer polymerization time may be used to achieved the same extent of surface grafting.

The method of contacting the surface-modified substrate and the reaction mixture containing the aniline or pyrrole monomer, oxidizing agent and doping agent may vary widely. One simple method involves soaking or dipping all or part of the substrate into the reaction mixture. The substrate is coated for a relatively short time. In general terms, the process of the invention is conducted to a point at which the polyaniline or polypyrrole film is still substantially transparent. With thicker coatings, the adhesion to the substrate becomes poorer. The thickness of the coating also depends on the composition and temperature of the reaction mixture and the coverage of the grafted copolymer on the substrate's surface. By way of example, the oxidizing agent may be ammonium persulfate or ferric chloride and the doping agent may be an inorganic or organic acid. In the case of polymerization of aniline, if the oxidizing agent used is ammonium persulfate, the preferred amount of the oxidizing agent is half of that of the aniline monomer on a mole basis. In the case of polymerization of pyrrole, if the oxidizing agent used is ferric chloride, the preferred amount is 2 times that of the pyrrole monomer on a mole basis. An oxidizing agent/monomer ratio substantially lower than those reported above will result in

slow or negligible polymerization whereas a substantially higher ratio is detrimental to the properties of the conducting polymer. A reaction temperature of not less than 0°C and not more than 50°C is preferred.

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 being limitations on the scope of the invention.

EXAMPLE 1

In a preferred experimental scale process, ozone pretreated polymeric substrates of 2cm x 5cm were immersed in 20ml of monomer solution in a Pyrex® tube. The concentrations of the monomer were varied from 2% to 25% (by weight). The most preferred concentration was 10%. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. The sealed tube was then immersed in a constant temperature bath maintained at 75°C for 0.5 to 2 hours. The reaction time was dependent on the reactivity of the monomer and the extent of graft copolymerization required. After each grafting experiment, the substrate was removed from the viscous homopolymer solution and washed with copious amount of deionized water. It was then subjected to repeated washing and soaking in a continuous stirred water bath for at least 24h at room temperature to remove the residual homopolymer. The surface modified substrate was subsequently dried by pumping under reduced pressure.

EXAMPLE 2

A piece of low density polyethylene (LDPE) film was graft copolymerized with acrylic acid (AAc) according to the procedure in Example 1 using 10% monomer solution and a polymerization time of 45 minutes. An 80ml solution containing 7.61g of p-toluenesulfonic acid monohydrate (TSA) and 0.46ml aniline in deionized water was prepared. Another solution of 20ml of deionized water, 1.90g of p-toluenesulfonic acid

and 0.57g of ammonium persulfate was then prepared and added to the first solution with vigorous stirring for a short period of time (about a minute). The AAc graft copolymerized LDPE film was then dipped into the solution. Within 30 minutes, a green transparent film was obtained and the film was lifted out of the solution and rinsed with 0.05M TSA solution to remove any clumps of bulk polymerized polyaniline on the substrate's surface. The film was then dried under reduced pressure for 2 hours. The surface resistance of the film was 6×10^3 Ω/sq. The adhesion of the polyaniline coating to the substrate was excellent and did not peel off by the application of Scotch tape. In contrast, a similar experiment conducted with a pristine LDPE film produced a thinner coating (i.e. lower absorbance) which was less conductive and peeled off readily with the application of the Scotch tape. The improved adhesion of the polyaniline coating on the AAc graft copolymerized substrate was retained even after heat treatment in air at 85°C or immersion in water for 24h.

EXAMPLE 3

A piece of LDPE film was graft copolymerized with AAc according to the procedure in Example 1 using 10% monomer solution and a polymerization time of 45 minutes. An 80ml solution containing 7.61g of TSA and 0.14ml pyrrole in deionized water was prepared. Another solution of 20ml of deionized water and 1.136g of ferric chloride hexahydrate was then prepared and added to the first solution with vigorous stirring for about a minute. The AAc graft copolymerized LDPE film was then dipped into the solution. Within a short period of time (less than 30 minutes) a dark coating was obtained. Experiments were carried out for different reaction times, after which the film was lifted out of the solution and rinsed with deionized water to removed any clumps of bulk polymerized polypyrrole on the substrate's surface. The film was then dried under reduced pressure for 2h. As in Example 2, for the same reaction time, the coating on the AAc graft copolymerized LDPE substrate was thicker, more conductive and adhered better to the substrate than that on pristine LDPE. The adhesion was the strongest for the coatings which are substantially transparent. Similar to Example 2, the adhesion of the polypyrrole coating to the substrate remained excellent even after heat treatment in air at 85°C or immersion in water for 24h.

EXAMPLE 4

Graft copolymerization of poly(ethylene terephthalate) (PET) films with sodium salt of styrene sulfonic acid (NaSS) was carried using a 10% monomer solution as described in Example 1 except near-UV light irradiation for 30 minutes was used instead of a heated water bath. After the grafting experiment, the PET film was treated as described in Example1.

For the polymerization of pyrrole, a solution of 6.5g of ferric chloride hexahydrate in 20ml of deionized water was added to a solution of 80ml of deionized water and 0.6ml of pyrrole with vigorous initial stirring. The NaSS graft copolymerized PET films was dipped into the reaction mixture maintained at 0 to 5°C. A dark coating was obtained within 5 minutes. The washing and drying procedure is as described in Example 3. For the same reaction time, a thicker, more conductive (by an order of magnitude) and more adherent polypyrrole coating was achievable on the PET film copolymerized with NaSS compared to that on the pristine PET film.

EXAMPLE 5

A piece of LDPE films was graft copolymerized with N,N-dimethyl acrylamide (DMAA) according to the procedure in Example 1, using 10% monomer solution and a polymerization time of 45 minutes. A polyaniline coating on the DMAA graft copolymerized LDPE substrate was obtained using the procedure described in Example 2. Under similar experimental conditions, the coating on the DMAA graft copolymerized substrate was thicker and more adherent than that on the pristine substrate but less so than that on the AAc graft copolymerized substrate (Example 2).

CLAIMS

We claim :

1. A method of enhancing the growth and adhesion of an electroactive polymer coating on a substrate which comprises the steps of :

   (a) surface functionalization via graft copolymerization of the substrate;

   (b) contacting said functionalized substrate with a reaction mixture of conjugated monomer, oxidizing agent and doping agent or counterion to form a coating of conjugated backbone polymer, and

   (c) removing the substrate from said contact after the formation of the conjugated polymer film.

2. The method according to claim 1, wherein said functionalization of the substrate is achieved first through pretreatment with gas plasma, ozone, corona discharge or UV-irradiation, followed by thermally or near UV-light induced surface graft copolymerization with polymerizable functional monomers.

3. The method according to claim 1, wherein said substrate is a polymer.

4.. The method according to claim 2, wherein the monomers for surface graft copolymerization are selected from the group of hydrophilic vinyl monomers, including the acrylic acid-based monomers, acrylamide monomers, sulfonic acid-containing monomers, and acrylate monomers.

5. The method according to claim 1, wherein the conjugated monomer is a substituted or unsubstituted aniline and said conjugated backbone homopolymer is a polyaniline.

6. The method according to claim 1, wherein the conjugated monomer is a substituted or unsubstituted pyrrole and said conjugated backbone homopolymer is a polypyrrole.

7. The method according to claim 1, wherein step (b) is carried out with a mixture of conjugated monomers and the said conjugated backbone polymer is a copolymer.

8. The method according to claim 1, wherein the conjugated polymer is electrically conductive.

9. The method according to claim 1, wherein the conjugated polymer is doped by one or more dopants.

10. The method according to claim 9, wherein the said dopants are inorganic or organic acids, acid derivatives or a combination thereof.

11. The method according to claim 9, wherein the said dopants are from the reaction mixture from step (b) in claim 1, functional groups graft copolymerized on the substrate surface or a combination thereof.

12. The method of claim 1 wherein said substrate is surface graft copolymerized in a predetermined pattern and the conjugated backbone polymer is formed on said surface of said substrate in said predetermined pattern.

13. The method of claim 1 wherein the enhancement of the adhesion of the electroactive polymer coating on the substrate is achieved and retained after prolonged heating in air or immersion in water.

14. An article comprising of a non-electrically conductive portion and an electrically conductive portion formed totally or in part using the method of claim 1.

15. A non-conductive polymeric substrate having an electrically conductive polymer coating on its surface, when prepared by a method as claimed in any one of claims 1 to 13.

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ABSTRACT

A method of enhancing the growth and adhesion of an electrically conductive polymer coating on a substrate which has been functionalized via graft copolymerization with hydrophilic monomers is described. The preferred substrates and the best advantages of the present invention are obtained with polymeric substrates which may be selected from but are not limited to polyolefins, polyesters, polycarbonates etc. The objects and advantages of the present invention are obtained by providing first a method for modifying the surfaces of the substrate. The preferred method of surface modification is via thermally or near-UV-light induced surface graft copolymerization of the pre-activated substrate surfaces with functional monomers. The functional monomers are selected from a family of vinyl monomers which readily undergo free-radical initiated polymerization, and more particularly, from the family of water-soluble or hydrophilic monomers such as but not limited to the acrylic acid-based monomers, acrylamide and acrylate monomers and sulfonic acid-containing monomers.