

PROCESS FOR BLACKENING A PLASTIC OR RUBBER MATERIAL

The present invention relates to a process for blackening a plastic or rubber material and, more particularly, to a process for blackening a plastic or rubber material by the incorporation of uniformly distributed nanoparticles of an electrically conductive polymer in a host polymer matrix.

Surface coating is, by far, the most common method used to colour plastic and rubber materials for aesthetic or protective purposes. Other, less commonly used methods, include the blending of dye pigments with the plastic materials or related prepolymers.

With regard to prior art blending methods, these have the disadvantage of only being applicable to thermoplastic polymers, because the polymers have to be softened (usually with the application of heat and pressure) before they can be blended with the pigments or dyes. Normally, after blending, the polymers then have to be vulcanised in order for them to take on their final shape, so that articles which have already taken on their final shape cannot be blackened by this method.

In the case of a black surface coating, the paint used normally comprises a mixture of black pigment, soluble polymer binder(s) and an organic solvent. Amongst the black pigments used, carbon black is of the most importance, because of its low cost. Other black pigments include graphite, black iron oxide ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), copper chromite ($2\text{CuO} \cdot \text{Cr}_2\text{O}_3$) and aniline black.

There are three major concerns associated with the use of a paint in surface coating of plastic and rubber materials. The first is the rheological property of the paint, which arises from the fact that the continuous phase of the paint is a polymer solution. Spray coating techniques, commonly used in industry coating lines, require non-dripping paints, i.e., polymer solutions of paints having a strong sheer-thinning effect. Such an effect can, however, have the drawback of non-uniform coverage of substrates having a complex geometry. The second concern relates to the properties of the black pigments used. Carbon blacks, for example, are often difficult to wet out and disperse in polymer solutions, due to the small particle size of carbon blacks (50-100nm) and the polar chemical groups held within the pigment surface. The degree of agglomeration of carbon black particles also affects dispersibility, viscosity and jetness of the paint, as well as gloss and wear resistance of the surface coating. The third concern is adhesion between the surface coating layer and underlying substrate, which has, for a long time, been a serious problem in the field.

Other previously reported blackening methods include the following two types of technique:

- (1) Introduction of oxidant, iron (III) chloride, into a polymer hydrogel via a swelling process, and exposure of the oxidant-loaded hydrogel to pyrrole or aniline.
- (2) Mixing pyrrole or aniline with monomers, and then subjecting the monomers to polymerisation. The resulting matrix, which traps the pyrrole or aniline monomers, is subsequently exposed to an oxidant.

In both methods, neither the oxidising agent or monomers can penetrate into the host polymer matrix, and polymerisation takes place at the interface between the liquid and host polymer, resulting in a surface film of polypyrrole or polyaniline only. The surface film of polymer coating has the same disadvantages of lack of uniformity and poor adhesiveness, as mentioned above. Method (1) also has the disadvantage that it is only applicable to hydrogel substrates, which do not normally have good mechanical properties in the dry state. Method (2) is, further, time consuming and tedious, and has a very narrow range of application, due to the negative effect that pyrrole and aniline have on the polymerisation process.

According to the present invention, there is provided a method for blackening a hydrophobic polymer matrix, which method comprises introducing monomers of an electrically conductive polymer into the polymer matrix, and polymerising the monomers in the polymer matrix in the presence of oxidant.

According to this method, the monomers are polymerised within the polymer matrix to form uniformly distributed nanoparticles of electrically conductive polymer. The nanoparticles alter the optical properties of the polymer matrix, to achieve a blackening effect, with little or no change to the mechanical and electrical properties of the host material, and because the nanoparticles are uniformly incorporated in the polymer matrix, the blackened material has excellent uniformity and adhesion properties. The degree of uniformity and adhesiveness that is achieved by the *in situ* polymerisation technique of the present invention cannot be achieved by prior art blending methods, and is also free of the disadvantages associated with prior art surface coating methods, in particular, the unfavourable rheological properties of paint and poor dispersibility of paint pigments.

The monomers of the electrically conductive polymer may be introduced into the polymer matrix before introduction of the oxidant. In this case, a surface layer of the polymer matrix is blackened.

In the case of surface blackening of the polymer matrix, the method of the present invention, preferably, comprises the steps of (a) immersing the polymer matrix in an organic solution of monomers and (b) immersing the monomer-loaded polymer matrix in an aqueous solution of oxidant.

Alternatively, the oxidant may be introduced into the polymer matrix before introduction of the monomers. In this case, the bulk of the polymer matrix is blackened.

In the case of bulk blackening of the polymer matrix, the method of the present invention, preferably, comprises the steps of (a) immersing the polymer matrix in an aqueous solution of oxidant and (b) immersing the oxidant-loaded polymer matrix in an organic solution of monomers.

The monomers for use in the methods of the present invention are, preferably, aniline or pyrrole monomers.

Preferably, the polymer matrix is a plastic material or a rubber material. Examples of rubber materials include butadiene-based rubbers, silicone rubbers, and polyurethane rubbers, all of which are suitable for use in connection with the present invention.

In the case of surface blackening of a polymer matrix, the polymer matrix is, preferably, a polycarbonate, such as poly(2,2-bis(4'-phenylene) propane carbonate, vulcanised NBR rubber (a copolymer of 1,3-butadiene, acrylonitrile and divinylbenzene), ABS (a block copolymer of acrylonitrile-butadiene-styrene), PVC, an acrylic plastic, a polyurethane, or a silicone rubber such as poly(dimethylsiloxane).

In the case of bulk blackening of a polymer matrix, the polymer matrix is, preferably, a silicone rubber.

According to another aspect of the present invention, there is provided a method of blackening the surface of a hydrophobic polymer matrix, which method comprises the steps of (a) introducing monomers of an electrically conductive polymer into the polymer matrix, (b) introducing oxidant into the polymer matrix, and (c) polymerising the monomers *in situ*.

According to a further aspect of the present invention, there is provided a method of blackening the bulk of a hydrophobic polymer matrix, which method comprises the steps of (a) introducing oxidant into the polymer matrix, (b) introducing monomers of an electrically conductive polymer into the polymer matrix, and (c) polymerising the monomers *in situ*.

Again, both these methods provide a means of blackening a plastic or rubber material, without affecting the mechanical and electrical properties of the material, and with the added advantages of high uniformity and excellent adhesiveness.

Preferably, the oxidant is produced by reacting $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with HCl having a concentration of approximately 2.5M or more.

Preferably, the oxidant is produced by reacting $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with a concentration of 2.5M to 12M HCl.

Presumably, the oxidant is Cl_2O according to literature a.J.D. Lee, Concise Inorganic Chemistry, 5th ed. Chapman & Hall, 1996, pp 609-610.

Also provided by the present invention is a hydrophobic polymer matrix prepared according to any one of the above-mentioned methods of the present invention, or by methods equivalent thereto.

According to a further aspect of the present invention, there is provided a hydrophobic polymer matrix containing nanoparticles of an electrically conductive polymer.

The nanoparticles of the electrically conductive polymer provide a blackening effect, with excellent uniformity and adhesive properties, and without affecting the mechanical and electrical properties of the polymer matrix.

Preferably, the electrically conductive polymer is polypyrrole or polyaniline.

The nanoparticles may be contained in a surface layer of the polymer matrix or, alternatively, the nanoparticles may be contained throughout the bulk of the polymer matrix.

Where the nanoparticles are contained in the surface layer of the polymer matrix, the polymer matrix is preferably a polycarbonate, vulcanised NBR rubber, ABS, PVC, an acrylic plastic, a polyurethane, or a silicone rubber.

Where the nanoparticles are contained throughout the bulk of the polymer matrix, the polymer matrix is, preferably, a silicone rubber.

In the case of blackening the bulk of a polymer matrix, the polymer matrix, preferably, contains less than 1% by weight of the electrically conductive polymer. Only a very small amount of electrically conductive polymer is required to achieve a blackening effect.

According to another aspect of the present invention, there is provided a method of producing an oxidant, which method comprises the step of reacting $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with HCl having a concentration of approximately 2.5M or more.

Preferably, the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is reacted with a concentration of from 2.5M to 12M HCl.

Also provided is an oxidant produced by such a method, or a method equivalent thereto.

According to a further aspect of the present invention, there is provided a molecule have the chemical formula Cl_2O .

The present invention, thus, provides a totally new way of chemically blackening plastic or rubber materials. Specifically, the present invention allows the incorporation of uniformly distributed nanoparticles of an electrically conductive polymer into a host polymer matrix, which is a totally different concept to conventional organic coatings and other prior art blackening methods.

The emphasis of the present invention is on a new approach for blackening plastic materials whose surface matrix can be swelled by monomers of certain conductive polymers, such as pyrrole or aniline. The blackening effect is achieved by the formation of uniformly distributed nanoparticles such as polypyrrole or polyaniline in the polymer matrix, by way of a simple immersion treatment, in specially formulated chemical baths. There are little or no changes in the mechanical or electrical properties of the host plastic or rubber articles. For some plastics, such as silicone rubbers, the blackening may be done throughout the entire bulk of the polymer matrix if desired, i.e., the present invention, in addition to providing a surface blackening technique, also provides a novel method of bulk blackening with a very low volume fraction of black pigment. Because nanosized particles, which impart the blackness to the surface or bulk of a plastic material, are embedded in the polymer matrix in a spatially uniform manner, the unique advantages of the methods of the present invention over conventional blackening methods include excellent uniformity, no adhesion problems, ease of application and low cost.

The methods of the present invention have the advantage over prior art blending methods, in that they may be used to blacken a finished article and, because the methods of the present invention do not need to use paint, they are free of all the disadvantages normally associated with the viscosity of paint and dispersibility of pigments.

With regard to prior art surface films, because the interfacial areas between the nanoparticles of electrically conductive polymer and the host polymer matrix in the present invention is very much larger than between a coating layer or surface film and its substrate, the result is a degree of adhesion in the present invention which is far beyond the reach of the coating layer or surface films of the prior art.

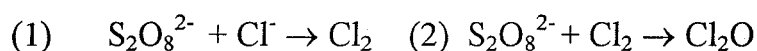
The methods of the present invention may, thus, be used to replace conventional blackening and paint coating processes to yield higher quality and lower cost plastic and rubber products. The methods of the present invention may be used to blacken any material comprising a hydrophobic polymer matrix, which includes the majority of engineering plastics.

In order that the invention may be more readily understood, and so that further features thereof may be more readily appreciated, examples of the invention will now be described by way of example only, with reference to the accompanying drawings, in which:

FIGURE 1 is a schematic illustration showing polymerisation of monomers of an electrically conductive polymer in a host polymer matrix.

The method of the present invention provides a totally new approach for blackening plastic and rubber materials, namely, the incorporation of nanoparticles of an electrically conductive polymer into the polymer matrix of a plastic or rubber material. The invention is based on a method of *in situ* polymerisation of monomers of an electrically conductive polymer in the host polymer matrix. In order to achieve this *in situ* polymerisation, the present invention provides a novel oxidant or oxidising agent, which is able to diffuse into the interstices of a host polymer matrix and initiate the polymerisation reaction.

The unique, small-molecular weight, oxidant species of the present invention is generated by reacting $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with HCl having a concentration of 2.5M or more, (preferably in the range of from 2.5M to 12M). Although not wishing to be bound by any theory of operation, it is believed that the reaction which takes place is as follows:



The oxidant that is generated by the above-mentioned reaction has the unique ability to diffuse into and permeate a hydrophobic polymer matrix. Prior art oxidants normally used for the preparation of electrically conducting polymers are not able to diffuse into the interstices of a hydrophobic host polymer matrix in this way, and so are unable to induce a blackening effect according to the methods of the present invention.

Because the oxidant, which initiates polymerisation, is able to diffuse into the matrix of a hydrophobic polymer, polymerisation of monomers can actually take place within the interstices of the polymer matrix. Normally, when monomers of an electrically conductive polymer are polymerised, the polymer particles tend to coalesce by a thermodynamically spontaneous process. However, when polymerisation takes place within the polymer matrix, the polymer matrix prevents the polymer particles from coalescing, resulting in the formation of nanoparticles of the electrically conductive polymer, uniformly distributed throughout the polymer matrix.

For some materials, the oxidant of the present invention is only able to diffuse into a host polymer matrix which already contains monomers of an electrically conductive polymer. For these materials, a surface blackening effect is obtained. Such materials include, for example, polycarbonates, vulcanised NBR rubber, ABS, PVC, acrylic plastics, polyurethanes and silicone rubbers.

For silicone rubbers, the oxidant of the present invention is able to diffuse into the host polymer matrix even in the absence of monomers of an electrically conductive polymer. For these types of materials, a blackening effect may be obtained throughout the bulk of the polymer matrix. Because silicone rubbers consist of alternate silicone and oxygen atoms, with two alkyl (or phenyl) groups attached to each silicone atom, it is believed that the structure allows itself to be penetrated more easily by hydrogen cations (H^+ , protons) than other polymers, via the formation of hydrogen bonds between the oxygen atoms and protons. The protonated matrix is then able to absorb the oxidant, which is a prerequisite for the bulk blackening process. Other matrixes having monomeric units with a high oxygen or nitrogen content, for example, polyurethane containing poly (ethyleneoxide) blocks, are also suitable for bulk blackening according to the methods of the present invention.

The present invention, thus, relates to two different methods for blackening plastic or rubber materials, both methods being based on the same principle of *in situ* polymerisation of monomers of an electrically conductive polymer in a host polymer matrix in the presence of oxidant (oxidation or diffusion polymerisation).

Examples of electrically conductive polymers that may be used in the methods of the present invention are polyaniline, polypyrrole and polythiophene, the corresponding monomers being aniline, pyrrole and thiophene, respectively. The preferred electrically conductive polymers for the purposes of the present invention are polyaniline and polypyrrole.

The electrically conductive polymers of the present invention are able to achieve a high quality blackening effect and, when used for blackening white, colourless or light-grey polymers, they provide a substantial difference in colouring.

In the case of surface blackening, the monomers of an electrically conductive polymer are first introduced into the polymer matrix by means of a swelling process. The polymer matrix is exposed to monomer, for example, by immersion in monomer liquid, or in an organic solution of the monomer. This allows impregnation of the polymer matrix, by diffusion, of molecules of monomer into the matrix surface, and the process may be applied to any plastic or rubber material whose matrix can be swelled by the relevant monomer. Matrixes that may be swelled by aniline or pyrrole monomers include matrixes that contain polar groups, such as a cyanide group, an ether group, or a siloxane group etc. The monomer-loaded polymer matrix is then exposed to oxidant, for

example, by immersing in an aqueous solution of the oxidant, or in an aqueous medium in which oxidant is produced *in situ*.

Thus, according to this process, pyrrole and aniline monomers are initially dissolved as a thin diffusion layer underneath the surface of the host polymer matrix, via a swelling process, and the pyrrole or aniline molecules are then polymerised *in situ* upon diffusion into the matrix of oxidant molecules, which leads to the formation of a black surface layer. The result is a very thin, blackened, diffusion layer, with excellent uniformity and adhesion properties.

In the case of bulk blackening, the above-mentioned process is reversed, and the polymer matrix is first exposed to oxidant, for example, by immersing in an aqueous solution of the oxidant, or in an aqueous medium in which the oxidant is produced *in situ*. Depending on the material used, oxidant is able to diffuse readily into the host polymer matrix. The oxidant-loaded polymer matrix is then exposed to monomer, for example, by immersing in monomer liquid, or in an organic solution of the monomer. Polymerisation occurs immediately upon diffusion of the monomer molecules into the matrix, and a blackening effect is obtained throughout the entire bulk phase of the plastic or rubber material.

In the case of silicone rubber, a shining blackened bulk silicone rubber matrix can be obtained with a content of polypyrrole or polyaniline of less than 1% by weight of the total weight content of the silicone rubber. One reason that a bulk blackening effect may be achieved on the basis of such a very low volume fraction of the black pigment, is that the particle sizes are very small, preferably in the range of 1-10 nm, and the spacial distribution of the particles in the matrix is close to perfect uniformity. Prior art techniques cannot reach such a goal. This is not only because the particle size of polypyrrole or polyaniline powder synthesised using normal methods is much greater than desired, but it is

also extremely difficult, if not impossible, to handle and add ultra fine powders into a vulcanised silicone rubber matrix uniformly by conventional compounding.

An example of a treatment liquid that may be used to generate the unique oxidant species of the present invention in the methods outlined above is an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml).

By selecting suitable reaction components and reaction conditions, the size and distribution of the nanoparticles may be controlled.

The illustrative methods and examples described herein are solely for the purposes of illustrating the present invention and are not intended to be construed as limiting.

Example 1

A piece of polycarbonate is immersed in a mixture of ethanol (4 parts), propanol (1 part) and aniline (4 parts) for 10 minutes and then taken out. The surface-attached solution is removed by rinsing the object with ethanol. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml). The above treatments are carried out at room temperature. The polycarbonate surface becomes black within a few minutes. The object is then washed in water and dried. The thickness of the black surface layer is about 10 μm and the texture is uniform.

Example 2

A piece of ABS is immersed in a mixture of ethanol (5 parts) and aniline (1 part) for 10 minutes and then taken out. The surface-attached solution is removed by rinsing the object with ethanol. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml). The above treatments are carried out at room temperature. The ABS surface becomes black within a few minutes. The object is then washed in water and dried. The thickness of the black surface layer is about 10 μm and the texture is uniform.

Example 3

A piece of PVC (polyvinylchloride) is immersed in aniline (1 part) for 60 minutes and then taken out. The surface-attached solution is removed by rinsing the object with ethanol. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml). The above treatments are carried out at room temperature. The PVC surface becomes black within 30 minutes. The object is then washed in water and dried.

Example 4

A piece of silicone rubber is immersed in a mixture of N-methyl-pyrrolidinone (5 parts) and aniline (5 parts) for 4 hours and then taken out. The surface-attached solution is removed by rinsing the object with ethanol. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30 g), HCl (12M, 30 ml) and distilled water (100 ml). The silicone rubber surface becomes black within a few minutes. The object is then washed in water and

dried. The thickness of the black surface layer is about 20 μm and the texture is uniform. The EDS surface elementary analysis shows that the surface black layer is a composite of silicone rubber and the Cl^- doped polyaniline. EDS (energy dispersive spectroscopy) can be readily used to determine the chemical composition of a surface layer (with a penetration depth of about 500-1000 nanometers).

Example 5

A piece of vulcanized NBA (butadiene-based) rubber sheet is immersed in a mixture of acetonitrile and aniline ($v/v = 1$) for 4 hours and then taken out. The surface-attached solution is removed by rinsing the object with acetone. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml). The NBA rubber surface becomes black within a few minutes. The object is then washed in water and dried. The thickness of the black surface layer is less than 5 μm and the texture is uniform.

Example 6

A piece of polyurethane elastomer sheet is immersed in a mixture of ethanol and aniline ($v/v = 5$) for 30 min and then taken out. The surface-attached solution is removed by rinsing the object with ethanol. After air-flow drying, the object is immersed into an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30g), HCl (12M, 30 ml) and water (100 ml). The polyurethane rubber surface becomes black within a few minutes. The object is then washed in water and dried.

Example 7

A piece of silicone rubber sheet (thickness = 5 mm) is immersed in an aqueous solution containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (30 g), HCl (12M, 30 ml), and water (100 ml) for 1 hour. An oxidant (which is believed to be dichlorine monoxide Cl_2O) is produced via a reaction involving the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and HCl with a trace amount of an initiator (Fe^{2+} , for example). This oxidant is able to penetrate into the matrix of the silicone rubber. The oxidant-loaded rubber is then taken out and rinsed with water to remove the surface-attached solution. The rubber is then immersed in a pure pyrrole liquid. It was observed that, only when the matrix traps the oxidant, can pyrrole be taken in. The oxidative polymerization of pyrrole takes place immediately as pyrrole molecules encounter the oxidant. As a result, black polypyrrole colloidal particles become embedded in-situ in the matrix. The colourless silicone rubber piece becomes entirely shining-black rubber.

Example 8

The experimental results listed in Table 1 show the following:

- (1) The oxidation systems of rows 2 and 4 are unable to achieve a blackening effect.
- (2) Only when HCl is being used can a blackening effect be obtained (comparing row 1 with row 3).
- (3) The concentration of HCl is crucial to the formation of the new oxidant Cl_2O (comparing row 1 with row 2).

Table 1 Influences of the reaction conditions

Oxidants	Concentration of Acid Solution	Occurrence of blackening
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	HCl(2.5M)-15ml	Yes
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	HCl(0.6M) - 21ml	No
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	H_2SO_4 (2.5M) - 25ml	No
FeCl_3	Without adding acid - 20ml	No

*3 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ acid and 6 grams of FeCl_3 was used respectively

In principle, the formation of one mole of Cl_2O consumes four moles of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and two moles of HCl. Accordingly, an excess of HCl is preferably used, to guarantee that the reaction takes place continuously until the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is used up. The amount of Cl_2O produced will also depend on the ratio of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to HCl. In the above examples, the initial molar ratio of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to HCl was maintained at 1: 2.8.

A variety of commercially available plastic or rubber products can be blackened using the methods of the present invention, at low cost, and by means of a very quick and simple treatment process.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

In the present specification "comprise" means "includes or consists of" and "comprising" means "including or consisting of".

CLAIMS

1. A method for blackening a hydrophobic polymer matrix, the method comprising:
introducing monomers of an electrically conductive polymer into the polymer matrix; and
polymerizing the monomers in the polymer matrix in the presence of an oxidant,
wherein the monomers are introduced into the polymer matrix before introducing the oxidant.
2. The method according to Claim 1, wherein the introducing and polymerizing comprises:
 - (a) immersing the polymer matrix in an organic solution of monomers; and
 - (b) immersing the monomer-loaded polymer matrix in an aqueous solution of oxidant.
3. The method according to Claim 1 or 2, wherein the monomers are aniline monomers.
4. The method according to Claim 1 or 2, wherein the monomers are pyrrole monomers.
5. The method according to any of Claims 1 to 4, wherein the polymer matrix is a plastic material.
6. The method according to any of Claims 1 to 4, wherein the polymer matrix is a rubber material.

7. The method according to Claim 1 or 2, wherein the polymer matrix is a polycarbonate, vulcanized NBR rubber, ABS, PVC, an acrylic plastic, a polyurethane, or a silicone rubber.
8. The method according to Claim 1 or 2, wherein the polymer matrix is a silicone rubber.
9. A method for blackening a hydrophobic polymer matrix, the method comprising:
 - introducing monomers of an electrically conductive polymer into the polymer matrix; and
 - polymerizing the monomers in the polymer matrix in the presence of an oxidant;
 - wherein the oxidant is introduced into the polymer matrix before introducing the monomers.
10. The method according to Claim 9, wherein the introducing and polymerizing comprises:
 - (a) immersing the polymer matrix in an aqueous solution of oxidant; and
 - (b) immersing the oxidant-loaded polymer matrix in an organic solution of monomers.
11. The method according to Claim 9 or 10, wherein the monomers are aniline monomers.
12. The method according to Claim 9 or 10, wherein the monomers are pyrrole monomers.
13. The method according to Claims 9 to 12, wherein the polymer matrix is a plastic material.

14. The method according to Claims 9 to 12, wherein the polymer matrix is a rubber material.
15. The method according to Claim 9 or 10, wherein the polymer matrix is a silicone rubber.
16. A method of blackening the surface of a hydrophobic polymer matrix, the method comprising:
 - (a) introducing monomers of an electrically conductive polymer into the polymer matrix;
 - (b) introducing oxidant into the polymer matrix; and
 - (c) polymerizing the monomers *in situ*.
17. The method according to Claim 16, wherein the monomers are aniline monomers.
18. The method according to Claim 16, wherein the monomers are pyrrole monomers.
19. A method of blackening the bulk of a hydrophobic polymer matrix, the method comprising:
 - (a) introducing oxidant into the polymer matrix;
 - (b) introducing monomers of an electrically conductive polymer into the polymer matrix; and
 - (c) polymerizing the monomers *in situ*;wherein the monomers are selected from the group consisting of aniline and pyrrole.

20. The method according to any one of the preceding claims, wherein the oxidant is produced by reacting $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with HCl having a concentration of approximately 2.5M or more.
21. The method according to Claim 20, wherein the HCl has a concentration in the range of 2.5M to 12M.
22. The method according to any one of the preceding claims, wherein the oxidant is Cl_2O .
23. The method according to Claim 2 or 10, wherein the aqueous solution of the oxidant comprises $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HCl (12M) and water.
24. The method according to Claim 16 or 19, wherein the polymer matrix is immersed in an aqueous solution of the oxidant, the aqueous solution comprising $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HCl (12M) and water.
25. A hydrophobic polymer matrix containing nanoparticles of an electrically conductive polymer, wherein the electrically conductive polymer is polyaniline.
26. The hydrophobic polymer matrix according to Claim 25, wherein the nanoparticles are contained in a surface layer of the polymer matrix.
27. The hydrophobic polymer matrix according to Claim 25 or 26, wherein the polymer matrix is a polycarbonate, vulcanized NBR rubber, ABS, PVC, an acrylic plastic, a polyurethane, or a silicone rubber.
28. The hydrophobic polymer matrix according to Claim 25, wherein the nanoparticles are contained throughout the bulk of the polymer matrix.

29. The hydrophobic polymer matrix according to Claim 25 or 28, wherein the polymer matrix is a silicone rubber.
30. The hydrophobic polymer matrix according to Claim 25, 28 or 29, wherein the polymer matrix contains less than 1% by weight of the electrically conductive polymer.