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Chemical deposition of conducting polymers

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Abstract

The coating of different materials with conducting electroactive polymers (CEP), i.e. polyaniline, polypyrrole, polythiophene, and their derivatives, provided by means of chemical polymerization, is briefly reviewed. The topics covered include the deposition of CEP (i) by bulk oxidative chemical polymerization, (ii) by surface-located polymerization, and (iii) by coating of micro- and nanoparticles. The coating of different materials like polymers, polymer particles, ion-exchange membranes, glass, fiber, textile, soluble matrices, inorganic materials is reviewed. The literature reviewed covers a 5-year period, beginning from 1995. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Polypyrrole; Polythiophene

1. Introduction

Conducting electroactive polymers (CEP) still remain a subject of intense investigation of many research groups worldwide. During the past decade, there have been many reports concerning fruitful investigations, leading to practical applications of CEP in various fields such as metallization of dielectrics, batteries, antistatic coatings, shielding of electromagnetic interferences, sensors and sensor arrays like electronic nose, etc. For many applications, two distinct ways of processing CEP are most frequently used:

1. Mechanical processing of CEP, obtained by chemical synthesis. However, almost all known parent (unmodified) CEP like polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT), have poor mechanical properties, they are insoluble, non-melting, and thus not processible. Therefore, some progress in mechanical processing was achieved by the use of mixtures of CEP with the usual processible polymer materials, as well as by the use of chemically modified CEP.
2. Coating of various materials, including plastics, glass, metals, as well as micro- and nanoporous materials, with a thin layer of CEP. Coating of polymer microparticles or latexes with CEP leads in some cases to composite materials that can be further mechanically processed to obtain bulk-conducting polymer composites. For many purposes, however, no bulky conduction is required; instead, a thin deposited surface layer of CEP is used.

The coating of various materials with a layer of CEP is achieved by the use of one of a few possible approaches.

1. Spreading of the solution of CEP on the surface of the material, followed by the evaporation of the solvent. Besides the difficulties concerned with the desired uniform coating of material surface with the solution of CEP, the main problem is the insolubility or even poor solubility of many CEP in nearly all solvents of practical interest. During the past years, some progress has been made in the chemical modification of the parent CEP structures to get more soluble polymer derivatives. For example, the introduction of an alkyl chain into the 3-position of pyrrole monomer, or of an alkoxy group into the *ortho*-position of the aniline monomer, yield upon polymerization the corresponding polymers that are more soluble in some organic solvents, whereas sulfonation of PANI enhances the solubility of the resulting polymer in water. However, the distortion of the molecular structure of CEP occurs upon such chemical modification, leading to a drastic decrease of the electric conductivity of the resulting polymers.
2. Electropolymerization of the monomers at electrodes, performed either in aqueous, or in organic solutions. Perhaps much of the knowledge on the polymerization mechanism and on the redox transformations taking place during reversible oxidation and reduction of CEP was obtained by the use of the electropolymerization

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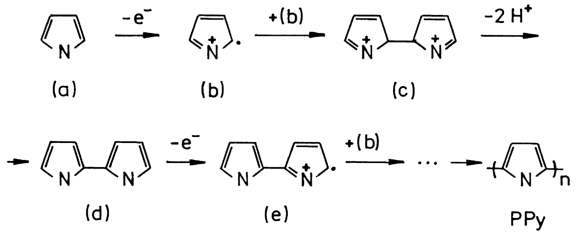

Fig. 1. Mechanism of oxidative polymerization of pyrrole.

procedure. However, electropolymerization is strongly restricted by the use of conducting materials, such as metals or carbon materials, whereas no electropolymerized CEP layers can be obtained on insulating surfaces.

3. Chemical polymerization, provided with relatively strong chemical oxidants like ammonium peroxydisulfate (APS), ferric ions, permanganate or bichromate anions, or hydrogen peroxide. These oxidants are able to oxidize the monomers in appropriate solution, leading to chemically active cation radicals of the monomers used. The cation radicals thus formed react with monomer molecules, yielding oligomers or insoluble polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids. However, a part of CEP, formed by chemical polymerization, can deposit spontaneously on the surface of various materials, immersed into the polymerization solution. The distribution of the resulting CEP between the precipitated and deposited forms depends on many variables and varies within a broad range. For the purpose of coating of materials with a layer of CEP, it is desirable to shift this distribution toward the surface-deposited form, whereas the bulk polymerization should be diminished as far as possible. This can be usually achieved by choosing the reaction conditions, like the concentration of solution components, the concentration ratio of oxidant to monomer, reaction temperature, and an appropriate treatment of the surface of the material to be coated by CEP. Although a bulk polymerization cannot be suppressed completely, a reasonably high yield of surface-deposited CEP can be achieved by adjustment of the reaction conditions.
4. Chemical polymerization, provided directly on the surface. In this case, the surface to be coated is enriched either with a monomer, or an oxidizing agent, and after that is treated with a solution of either oxidizer or monomer, respectively. A major advantage of this process is that the polymerization occurs almost exclusively at the surface, whereas no bulk polymerization in the solution takes place. For some polymer materials, the surface can be enriched with a monomer by its sorption from solution. The enrichment of the surface by an oxidizer can occur either by ion-exchange mechanism, or by the deposition of an insoluble layer of oxidizer. The disadvantage of this process is that it is limited by materials that can be covered or enriched with a layer of either monomer or oxidizer in a separate stage, preceding the surface polymerization.

In the present work, the coating of different materials by the means of chemical polymerization is reviewed. As far as possible, the deposition of CEP by bulk polymerization, and by surface-located polymerization, is reviewed separately. A separate section is devoted to the deposition of CEP on micro- and nanoporous materials, provided either by bulk, or by surface polymerization process. The literature reviewed covers a 5-year period, beginning from 1995. A number of valuable reviews on the coating of materials with CEP, chemical polymerization, and some related topics have been published in the past 5 years. De Jesus et al. reviewed conductive polymer blends, prepared by in situ polymerization of pyrrole within another polymer matrix [1]. Conducting PANI blends and composites, their synthesis by oxidative polymerization and processibility were reviewed by Anand et al. [2], and Bhattacharya and De reviewed both PANI- and PPy-based composite materials [3]. The same authors reviewed more specific topics on the modification of the structure of CEP to increase their solubility and processibility [4]. A review on PANI synthesis by oxidative polymerization was presented recently by Gospodinova and Terlemezyan [5]. The use of CEP in a specific field of shielding of electromagnetic interference was reviewed by Huang [6]. The present short work, I hope, will provide an access to the literature of the past years on the deposition of CEP by means of chemical oxidation.

2. Deposition of CEP by bulk chemical polymerization

Many well-known chemical oxidants are able to oxidize monomers like aniline or pyrrole, yielding highly active intermediate species like their cation radicals, thus initiating the polymerization process. Once formed, intermediate species react with solution monomer molecules, yielding dimers, oligomers, and polymers as end products of oxidative polymerization. Fig. 1 shows schematically the process of polymerization of pyrrole. A neutral molecule of pyrrole monomer (a) yields upon its oxidation cation radical species (b), that can recombine, yielding consecutively a dication of bipyrrole (c), and, after its disproportionation, a neutral bipyrrole molecule (d). The latter can undergo further oxidation (e), deprotonation and recombination steps, leading to PPy as the end product of oxidative polymerization.

The formation of intermediate species such as cation radicals has been evidenced in many works dealing with the polymerization of some monomers. Fig. 2 shows UV–Vis spectra for electro-oxidation of *N*-ethylaniline, provided in an acidic solution of this monomer at indium-doped tin oxide (ITO) transparent electrode. After application of a suitable electrode potential, two absorbance bands appear in the spectrum, and a continuous growth of their intensities is observed during electrolysis. After interruption

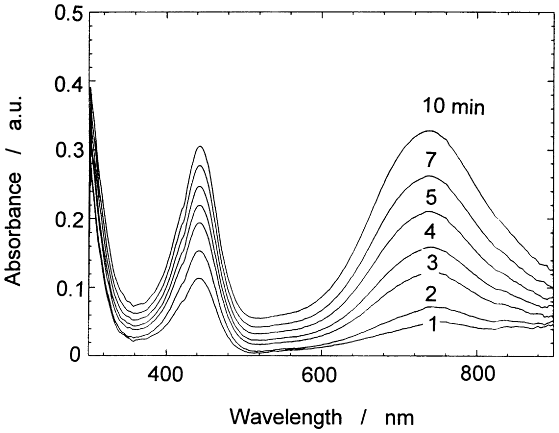

Fig. 2. UV–Vis absorbance spectra, obtained at transparent ITO glass electrode in a solution of 0.5 M H_2SO_4 containing 25 mM of *N*-methylaniline, by applying the electrode potential of 1.0 V vs. NHE, as recorded at different time moments (as indicated, in minutes).

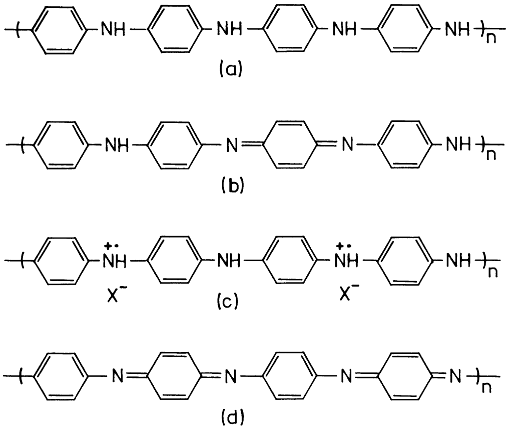

Fig. 4. Different redox forms of polyaniline: (a) leucoemeraldine base (reduced form), (b) emeraldine base (half-oxidized form), (c) conducting emeraldine salt (half-oxidized and protonated form), and (d) pernigraniline base (fully oxidized form).

of electrolysis, the band at ca. 450 nm decreases gradually and disappears in a few minutes, indicating clearly its origin from intermediate species, formed during electrolysis. At the same time, the band at ca. 740 nm continues to grow to some extent, indicating its origin from an end product of electro-oxidation.

The process of the chemical oxidative polymerization is usually followed by visible changes in the color of the polymerization solution. An initially colorless solution turns, after a definite time, blue and dark blue, indicating that di- and oligomers are to be formed. Some time later, the precipitation of a dark blue or black solid polymer is observed. In most cases, the chemical polymerization possesses a well-defined autocatalytic character, i.e. a rapid coloration and polymerization proceeds after a definite induction period. The rate of the process depends upon many variables, such as the nature of oxidant used, and the concentration of reactants [7,8]. Usually, most of the CEP formed by the chemical polymerization precipitates after the reaction is completed. However, a part of the CEP can spontaneously deposit as a thin layer on various substrates present in a reaction medium.

Many CEP can exist in a variety of their redox forms; however, the electric conductivity is assigned usually to only one of them. For example, the withdrawal of one electron from the PT molecule (Fig. 3a), followed by its doping with a solution anion, leads to its conducting half-oxidized polaronic state (b), whereas the loss of the second electron leads to the oxidized bipolaronic form (c). Similarly, only the half-oxidized, protonated and anion-doped emeraldine form of PANI (Fig. 4) shows high electrical conductivity, whereas other redox forms like the reduced leucoemeraldine form (a) have low or no conductivity. On an electrochemical potential scale, the regions of the existence of different redox forms depend greatly on the nature of CEP, the acidity of the solution, and other variables. Fig. 5 shows a cyclic voltammogram for PANI in an acidic aqueous solution. Two pairs of anodic and cathodic current peaks are seen clearly, centered at around 0.3 and 0.9 V vs. NHE. At lower electrode potentials, not exceeding ca. 0.3 V, the reduced (leucoemeraldine) form prevails, whereas at high potentials, exceeding ca. 0.9 V, the fully oxidized (pernigraniline) form exists, leaving a broad potential window, ranging from 0.3 to 0.9 V, where the conducting emeraldine form is most stable. The redox transitions between these forms can be driven not only by changing the electrode potential, but also by using suitable chemical oxidation or reduction agents.

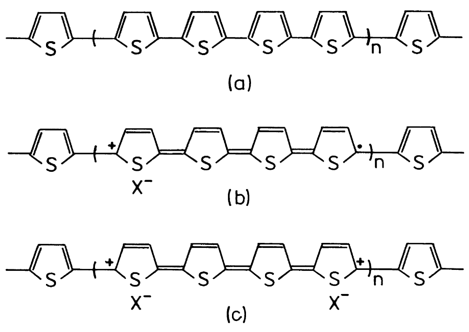

Fig. 3. Different redox forms of polythiophene: (a) reduced, (b) half-oxidized (polaronic), and (c) oxidized (bipolaronic).

Besides electric conductivity, different redox forms of CEP differ in many of their physicochemical properties. Fig. 6 shows UV–Vis absorbance spectra for PANI film in its three different oxidation states. A relatively low absorbance in the visible region for the reduced form, corresponding to its colorless or slightly yellow appearance, changes drastically by moving to the half-oxidized emeraldine state. The latter has an intense and broad absorbance band in the red region of the visible spectrum, determining an intense green or blue color of this redox form. Further oxidation of this form to a fully oxidized pernigraniline state causes a shift of the absorbance band towards lower wavelength, resulting in a corresponding color change.

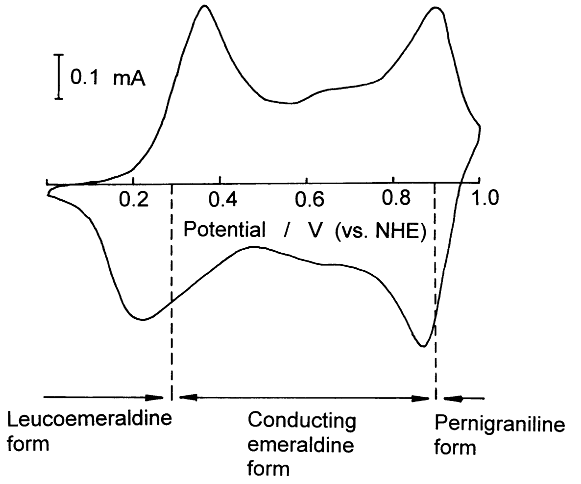

Fig. 5. Cyclic voltammogram of polyaniline-coated platinum electrode, obtained in 0.5 M H_2SO_4 with potential scan rate of 0.1 V/s, indicating electrode potential range, where different redox forms exist.

The presence of an intense light absorption band in the spectrum of both half-oxidized and fully oxidized forms of PANI enables one to follow the process of chemical polymerization by spectral means. Fig. 7 shows spectrokinetic curves for oxidative polymerization of aniline with the use of dichromate anion as oxidant. A well-defined induction period is seen for nearly all combinations of aniline and oxidant concentrations. During this period, almost no increase of light absorption is observed. Depending on the reaction variables, this induction period varies between a few and a few tens of minutes. After that, a fast coloration of the reaction mixture proceeds, indicating some oligomers or polymers to be formed. Later, these polymers deposit onto the walls of a reaction vessel, or precipitate as an insoluble solid. The rate of polymerization depends greatly on the concentration of both the monomer and the oxidant, as depicted in Fig. 7 for different concentrations of both reaction components.

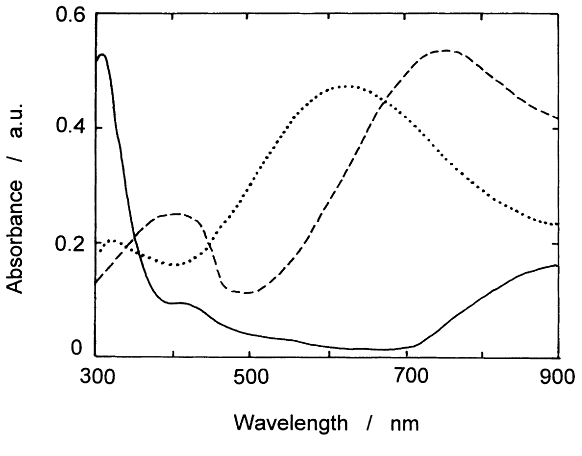

Fig. 6. UV–Vis spectra of polyaniline: solid trace — in its reduced (leucoemeraldine), dashed trace — half-oxidized (emeraldine), and dotted trace — fully oxidized (pernigraniline) forms. Spectra were obtained in 0.5 M H_2SO_4 for thin polymer film, deposited on the glass surface.

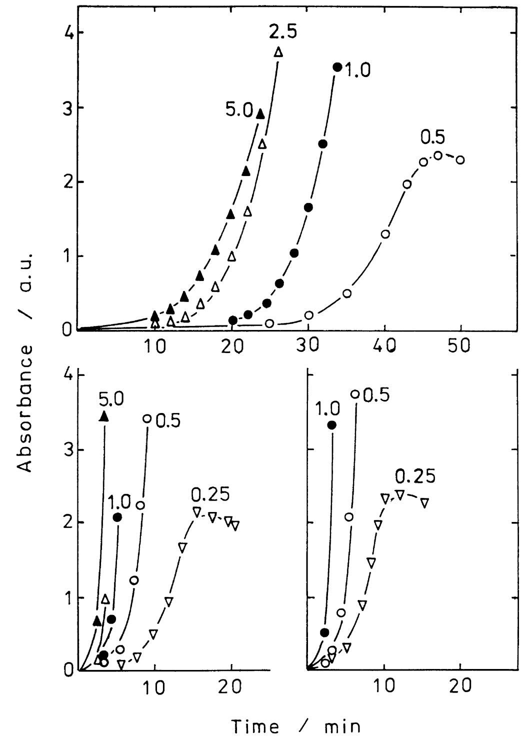

Fig. 7. Photometric kinetic curves of aniline oxidation, obtained at 700 nm in a 10-mm path length quartz cuvette, containing a solution of 0.5 M H_2SO_4, 10 mM (top), 50 mM (bottom left), or 100 mM (bottom right) aniline, and different concentrations of potassium dichromate (as indicated at corresponding curves, in millimolar).

Polymerization in the bulk of the solution appears unfavorable for the purpose of the deposition of CEP on the surface. Although the polymerization in the bulk cannot be excluded completely, it can be suppressed to an appropriate level, and some works in the field address this problem. A useful example of the optimization of deposition was presented by Saurin and Armes [9] for the deposition of PPy onto printed circuit boards (PCBs) for electroplating applications. The use of a relatively mild oxidizer, a complex of Fe^{3+} ions with 5-sulfosalicylic acid instead of simple Fe^{3+} ions, a high oxidant to monomer ratio, and the optimization of coating procedures enabled to coat a large number (at least 15) of PCBs in the same polymerization bath, maintaining at the same time the quality of the PPy coating.

2.1. Polymers

A wide variety of materials were coated with thin layers of CEP. A large number of papers report the deposition of CEP onto relative smooth polymer and related surfaces of relatively large area. Both aniline and pyrrole were involved in the coating, and a number of oxidants were used in polymerization.

Transparent and conducting coatings of PANI on polymethylmethacrylate (PMMA) and polyvinylchloride were obtained by chemical oxidative polymerization, and the influence of component concentration and polymerization time was studied, enabling to obtain PANI films with a surface resistance of 10^3–10^4 Ω/square and transparency of 60–70% [10]. Silane-modified substrates were coated with a PANI layer, provided by dipping into an acidic solution of aniline with subsequent addition of ammonium persulfate into the reaction solution [11]. The resulting PANI films had good order and adhesion, and their thickness and conductivity can be varied by varying the polymerization conditions. For the film of 1 μm thickness, a conductivity of 0.5 S/cm was reported, which is close to that of a compressed pellet of PANI [11]. Coatings of PANI and PPy were obtained on low-density polyethylene (LDPE) and the surface of the substrate was pointed out to play a major role in determining the growth and adhesion of the film [12]. It was found that LDPE grafted with acrylic acid enhances the growth of the films, and that both acrylic acid and *N*,*N*-dimethylacrylamide graft copolymerized substrates promote the adhesion of CEP films [12]. Graft copolymerization of LDPE, high-density polyethylene (HDPE), polypropylene, poly(ethylene terephthalate) and polytetrafluoroethylene with acrylic acid and sodium styrenesulfonate was reported to yield functionalized surfaces that can be coated with a layer of PANI [13]. Interpenetrating conductive polymer networks, consisting of PANI and cross-linked cellulose, were prepared by oxidative polymerization of aniline within the self-synthesized cellulose network [14]. The conductivity of the prepared polymer network increased with an increase in aniline content, HCl to aniline ratio, and reaction time during polymerization, and was found to be much greater than for PANI/cellulose acetate composite [14]. The formation of the conducting PANI/poly(ethylene terephthalate) composite has been shown to proceed in Cl_2 (or Br_2) containing water medium [15]. The possibility of grafting between CEP and insulating polymers, such as poly(bisphenol carbonate) and polyamide, was investigated also by theoretical semi-empirical methods [16].

Some work was done on the coating of thin polymer films with a layer of PANI. The polymerization of aniline with the use of ammonium persulfate on biaxially stretched polypropylene microporous films gave PANI/polypropylene composites, whose electric conductivity can be controlled over a wide range [17]. Under proper conditions, flexible and strong enough films with conductivity of 5–6 S/cm were prepared [17]. A conducting transparent polymer film was prepared by a dipping polymerization, showing the conductivity of 1–5 S/cm and transmittance of 80% at 450–650 nm for 0.5 μm PANI layer [18]. PANI and PPy thin films, obtained by the chemical polymerization, showed some loss in conductivity, but no deterioration in optical transparency during weathering, salt fog and humidity exposure [19]. Besides aniline, some of its derivatives, like *o*-toluidine and *o*-chloroaniline were polymerized on polypropylene microporous film, resulting in lower electric conductivity, as compared to a similar PANI composite film [20]. The preparation of PANI and PPy layers on the conventional polymers with the next following electrodeposition of copper onto the composites with the aim of metallization of polymers was reported [21].

Besides PANI, PPy is also often used in coating of plastics and related materials. Plastic supports such as polyester membranes and polystyrene slides were coated with PPy by the use of Fe^{3+} ions as oxidizer, and the resulting composite showed changes of the NIR spectra with pH and on exposure to NH_3 vapor, useful for sensing purposes [22]. Graft copolymers of pyrrole and 3-alkylpyrroles with methylmethacrylate and some other methacrylates were prepared by chemical oxidation with $FeCl_3$ [23]. The conductivity of the resultant graft copolymers attained 10^{-4}–10^{-3} S/cm. The graft copolymers of 3-alkylpyrroles were reported to be completely soluble in common organic solvents even in their doped state, in contrast to graft copolymers of pyrrole [23]. PPy was chemically synthesized by oxidation with Fe^{3+} perchlorate on one side of non-woven fabric for use as an electrode, showing a high electric capacity of 72 mA h/g [24]. Smooth films of PPy were synthesized on various substrates by the use of ammonium persulfate as well [25]. The relationship between the structure, conductivity and optical absorption in the NIR region was investigated for chemically deposited thin films of PPy on various substrates, and it was concluded that conductivity and adhesion could be optimized by tuning the hydrophobicity of the substrate surface [26]. Composites of PPy in host matrices of polyacrylic acid and bisphenol A based epoxy have been prepared by chemical polymerization, and their characteristics have been compared with similar composites, prepared by dispersion of PPy [27]. Conductive PPy–polyurethane foam was prepared by polymerization of pyrrole using mixtures of $FeCl_2$ and $FeCl_3$ as oxidant, and the conductivity of the foam was found to increase with increasing $FeCl_2/FeCl_3$ ratio, increasing oxidant content, and decreasing reaction temperature [28]. The procedure for preparing conducting membranes by chemical polymerization of pyrrole in the pores of the macroporous membrane was reported [29]. Ultrathin PPy films of nanometer thickness were obtained by repeating adsorption of PPy from the polymerization solution, and the thickness of the PPy film was found to increase linearly by using a fresh polymerization mixture at each adsorption step [30]. It was shown that the polymerization of pyrrole onto polymeric track-etched membranes occurs both on the pore walls and on the face surface of the membrane, leading to a gradual decrease of the pore size during polymerization [31]. PPy films, prepared by polymerization in the self-assembled arrays were characterized and compared with samples, prepared by polymerization in the absence of self-assembled arrays, showing differences in conductivity and stability [32]. Fine CEP patterns were prepared on plastics and other materials by UV irradiation of polymerization solution, containing photoreactive oxidizers like $FeCl_3$ [33]. These salts are reduced by exposure to UV light, thus losing their ability for oxidation polymerization; therefore, conducting PPy patterns can be obtained on the unradiated parts [33].

2.2. Glass

A great deal of attention has been paid in recent years to coating glass and some related inorganic substrates with thin layers of CEP. On a smooth surface of glass, poor adhesion of CEP is usually obtained; thus, the increase of adhesion of CEP to the surface is the main problem in coating of smooth substrates like glass.

PANI coatings on glass can be obtained by simple immersion of the glass substrate into the polymerization solution, containing aniline and ammonium persulfate [34]. For these films, a linear relation of their thickness and optical density was found by the use of optical interferometry, whereas the electric conductivity of the films and of bulk PANI produced simultaneously was the same [34]. The thickness of the deposited films can be varied by varying the duration of the substrate dipping. A film of a thickness of 30 nm was obtained during a dipping time of 5 min, for example [35]. For this film, surface roughness of ca. 3 nm was estimated by atomic force microscopy, and the conductivity of 2–6 S/cm was determined using a four-probe measurement approach [35]. Film morphology and mechanical elasticity can be varied by deposition of CEP composites, or CEP layer doped by polyanionic dopands. PANI–polyacrylic acid composite thin films were deposited by oxidation with ammonium persulfate of a reaction mixture, containing aniline and polyacrylic acid [36], and some spectral and conductivity differences were found for this composite. Composite films of PPy and phosphomolybdic acid of 40–100 nm thickness have been deposited by chemical polymerization using the spin coating procedure, showing a conductivity of 15–30 S/cm [37]. Some attempts have been made to increase the adhesion and improve the texture of the deposited films [38]. An increase of surface adhesion was achieved by the modification of the surface prior to chemical polymerization. For this modification, a silane-compound-bearing pyrrole group was used, which attached to the SiO_2–Si surfaces via self-assembly, forming a monolayer of silane-bearing pyrrole molecules on the surface [39]. PPy films, obtained on these modified surfaces, had a thickness of 40–550 nm, and adhered firmly to the surface [39]. Patterned self-assembled monolayers of octadecylsiloxane were generated on the hydroxyl-terminated surfaces like glass by microcontact printing, defining and directing the deposition of CEP [40]. The rate of deposition was greater on the hydrophobic surface. The polymer deposited on the hydrophobic surface had a more extended conformation, and thus a higher conductivity, than that formed on the hydrophilic surface [40].

2.3. Polymer particles

Various small particles, mostly polymer ones, were reported to be coated with a layer of CEP, mainly with the aim of further processing, e.g. by melting to get bulky conductive composite materials. PPy coatings were obtained by oxidation of pyrrole with $FeCl_3$ in water–methanol mixtures on polypropylene particles 35 μm in diameter, varying the content of PPy in a resulting composite from 1.1 to 10.4 wt% [41]. The modified powder was then compression molded to yield polypropylene/PPy composite films of about 0.2 mm thickness, having an electric conductivity ranging from 4×10^{-10} to 5×10^{-3} S/cm, which is ca. 7 orders of magnitude higher than the conductivity of the blends prepared by mechanical mixing of polypropylene and PPy in the same PPy content range [41]. Highly conductive composites were also prepared from a mixture of coated and uncoated polypropylene particles [42], and some modifications of this procedure were reported [43,44]. The same authors extended this procedure of coating to other polymer–PPy composites [45,46].

Copolymers based on polystyrene and having pyrrole moiety were prepared by emulsion polymerization, and pyrrole was coupled onto these copolymers by oxidative polymerization using $FeCl_3$ in the emulsion, yielding a composite of high conductivity (1.5 S/cm) [47]. PPy was polymerized on PVC powder dispersed in an aqueous solution of $FeCl_3$, and the resulting PPy-encapsulated PVC particles were compression molded into a conductive composite material [48]. For this material, a very low percolation threshold value of 0.3 wt% was reported, whereas the conductivity can be at least 10 orders of magnitude higher for samples containing 1.6 wt% of PPy, as compared to a pure PVC sample [48]. Similarly, particles of sulfonated polystyrene were coated with PANI by oxidative polymerization using ammonium persulfate, and the resulting PANI-coated particles were found to be of higher dispersibility than PANI itself in an organic solvent [49]. Through a chemical polymerization of pyrrole with $FeCl_3$ inside of the ultrahigh molecular weight polyethylene foam, a conducting polymer foam was prepared [50].

2.4. Fiber and textile

Chemical oxidative deposition of CEP onto different kinds of fiber and textile yield new composite materials that are expected to have potential use in various fields.

A PPy–carbon fiber composite with a carbon fiber content of 15–20% was prepared by the chemical polymerization of pyrrole [51]. The resulting composite has high tensile strength and good thermal stability, and can be used as a cathode material for a rechargeable battery, where carbon fibers act as an electrically conductive skeletal electrode for current collection with a specific capacity of 91 mA h/g [51]. Besides conducting carbon fiber, non-conducting fibrous materials can be extended to surface polymerization of CEP. Graft copolymerization of PANI and poly(*o*-toluidine) onto poly(ethylene terephthalate) fiber was achieved by the use of persulfate as polymerizing agent [52]. The conductivity of a composite containing insulating polymer fiber coated with PPy was found to increase by more than 10 orders of magnitude above some threshold concentration [53].

Textile substrate was covered with PPy layer by its immersion into the polymerization solution, and the gradual loss of conductivity of the resulting composite was shown to proceed much faster in the presence of oxygen, than in its absence [54]. A possible application of this material in microwave attenuation, EMI shielding, and static electric charge dissipation was pointed out [54]. Although a number of problems should be solved, relating to optimization of CEP deposition, or environmental stability of these composite materials, their microwave absorption characteristics make them useful for military applications like camouflage and stealth technology [55]. Thus, a patented process of PPy deposition on textiles of all kinds, and a pilot device for the industrial upscaling have been described [56]. Many characteristics of CEP-coated textiles can be improved by known means. Thermal stability of the PPy coating on the textile was improved by the incorporation of aromatic dopants, such as anthraquinone-2-sulfonate, or of small quantities of benzophenone-based stabilizing agents [57].

Some fibers and textiles can be coated by CEP layers by immersing them into an electrolyte, where electrochemical polymerization takes place. The electrochemical grafting of PANI onto cotton, silk and wool fibers was reported [58], provided by subjecting them to electrical treatment in the electropolymerization solution in aqueous *p*-toluenesulfonic acid electrolyte. During electrolysis, the weight of the fibers increased monotonically, and their electrical resistivity decreased [58,59]. The conductivity of the composite materials thus prepared was found to vary between 0.2 and 15 S/cm, depending on the nature of the fibers, and coating procedure [60].

2.5. Soluble matrices

Because of poor stability of nearly all CEP in water or organic solvents, some attempts have been made to polymerize some monomers such as pyrrole onto soluble matrices. A number of matrices, including those containing multiple negative charge, thus enabled us to obtain polymer-doped CEP, and various oxidizers were used in the matrix polymerization. Depending on the reaction conditions, both insoluble and soluble composite materials can be prepared. Between these, soluble complexes seem to be more attractive, since they can be cast onto various substrates, yielding a conducting layer of CEP upon evaporation of the solvent.

By means of chemical polymerization, provided with the use of $FeCl_3$ oxidant, pyrrole was polymerized in PMMA matrix dissolved in ethyl acetate, and a soft free-standing composite film was obtained by evaporation of the solvent, having a conductivity about 3 S/cm (for the film with 40% PPy content) [61]. Water-soluble products along with insoluble products were obtained by oxidative matrix polymerization of pyrrole with Fe(III), Ni(II), Co(II) and Cu(II) ions in the presence of polyacrylic acid, and ternary complexes consisting of PPy, polyacrylic acid and metal ions were found to form by different methods [62]. Similarly, water-soluble and insoluble products were obtained by matrix polymerization of pyrrole by Ce(IV) ions in the presence of polyacrylic acid [63]. Composite films of PPy and poly(ether urethane) were prepared by the polymerization of pyrrole with $CuCl_2$ in the presence of lithium perchlorate in a tetrahydrofuran solution, and subsequent casting [64]. The conductivity of the resulting film was 0.16 S/cm in the direction parallel to the film surface, but very low conductivity of 8×10^{-7} S/cm was obtained in the direction perpendicular to the film surface, which was attributed to the ionic conduction of the PEU–$LiClO_4$ component, with little contribution from the electronic conductivity of the PPy component [64]. Conducting PANI–polystyrene composites were prepared by the oxidation of aniline solution in xylene, containing PS and dodecylbenzenesulfonic acid [65]. As PANI content in the composite increased up to 12%, the conductivity increased up to 0.1 S/cm [65]. Water-soluble PPy graft copolymers with polyamines or polyimines were obtained in an acidic solution with the use of $FeCl_3$ or ammonium persulfate as oxidant, showing semiconductivity in the undoped state [66]. Pyrrole was grafted onto a PMMA backbone which contains the pyrrole moiety, via oxidative polymerization with $FeCl_3$ in nitromethane [67]. The solubility of the resulting graft copolymers in water decreased with increasing pyrrole content owing to the formation of long PPy chains. Graft copolymers of aniline onto the backbone of polyacrylamide were obtained via polymerization with ammonium persulfate in aqueous acidic solution [68]. At low aniline to acrylamide ratio, the copolymer can be dissolved in 5% NaOH solution, and after removal of the salt ions by dialysis and evaporation of the solution, a thin film of PAM-*g*-PANI can be obtained and doped with HCl, showing a high conductivity of 8.8 S/cm [68]. The oxidative polymerization of aniline or pyrrole with phosphomolybdic acid $H_3PMo_{12}O_{40}$ was performed, resulting in a hybrid material, possessing good conductivity in combination with the added electroactivity of the inorganic cluster, which is strongly anchored in the polymer and cannot be exchanged upon reduction [69].

3. Deposition of CEP by surface polymerization

The well-known process of metallization of PCBs still remains one of the most successful practical applications in deposition of CEP by chemical polymerization, provided on the surface of insulating materials. This process has been offered in the market since the early 1990s. In this process, the surface of a PCB is first treated with alkaline permanganate solution, and a layer of manganese dioxide is deposited selectively on the plastic parts of the PCB. Then, a thin layer of PPy is deposited onto the PCB by treating it with an acidic solution of pyrrole, where the polymerization of pyrrole by manganese dioxide proceeds. After that, a layer of copper metal is deposited on the PPy-coated PCB by electrodeposition. In the past few years, continuing interest has been paid to the deposition of CEP by the surface polymerization process, and a wide variety of materials have been involved in these processes.

3.1. Polymers

The coating of polymers, as well as of a number of other materials with a layer of CEP by surface polymerization can be performed either by first fixing of a monomer layer onto the surface, followed by polymerization in an oxidant solution, or, alternatively, by first enrichment of the surface by an oxidant, followed by polymerization in a monomer solution. Both of these possibilities are attracting considerable interest.

PANI–nylon 6 composite film was prepared following a diffusion polymerization method by immersion of 10 μm thick nylon-6 films, enriched with aniline, into an ammonium persulfate solution [70]. The resulting composite film showed high conductivity and low percolation threshold contents of PANI of ca. 4%. Conducting composites of porous cross-linked polystyrene as host polymer and polybisthiophene were synthesized in the vicinity and above the percolation threshold by the action of $FeCl_3$ solution on porous polystyrene initially charged with 2,2′-bithiophene [71]. Coating of polyimide films with a layer of PPy or poly(3-methylthiophene) (PMT) was performed by soaking the films in the corresponding monomers for 24–72 h, where a monomer uptake of 11–14% for pyrrole, or 8–11% for 3-methylthiophene was achieved, followed by polymerization in a solution of anhydrous $FeCl_3$ in acetonitrile [72]. The conductivity of the composite reached 5.7 S/cm for PMT, or 0.041 S/cm for PPy, and a good long-term stability of the composites was found upon storage in air under ambient temperature for 300 days [72]. PANI composites with PMMA and PS were obtained by polymerization of the corresponding monomers, previously embedded in an insulating polymer matrix, in an atmosphere saturated with an aqueous solution of HCl and ammonium persulfate [73]. The low percolation threshold obtained was attributed to a fiber structure of the PANI phase inside the composite materials. The synthesis of a PPy film on non-conducting substrates was provided by dipping the substrate in a pyrrole solution and subsequently in an oxidizing solution containing $Fe(ClO_4)_3$ [74]. PMMA–PANI conducting films were prepared by the diffusion–oxidation method with the use of $FeCl_3$ oxidant, resulting in the reduction of the resistivity of the films from 10^{13} to 10^3 Ω cm [75]. Premolded films of the sulfonated polystyrene ionomer were coated with PPy by sequential immersion in aqueous solution of pyrrole and $FeCl_3$ [76]. The amount of PPy produced, as well as the penetration of PPy into the film depend on the immersion time of the film in the monomer, and the degree of sulfonation of the ionomer. Surface conductivities ranging between 10^{-4} and 10^{-1} S/cm were reported for PPy concentrations ranging between 2 and 22% for a 15 μm thick film [76]. Conducting polychloroprene–PANI composites were prepared by swelling the vulcanized rubber material in aniline followed by immersing into aqueous solution containing HCl and ammonium persulfate [77].

Besides sorption and swelling, some different methods were reported to enrich the surface layer of a polymer with polymerizable monomer. Aniline was dispersed in PMMA and polyvinylcarbazole solutions, the resulting mixtures were coated on substrates, dried, and then exposed to an atmosphere of HCl and ammonium persulfate, yielding stable PANI coatings [78]. Polyurethane films containing 3-methylthiophene were prepared by the condensation of poly(propylene glycol)diol, poly(propylene glycol)triol, and toluene 2,4-diisocyanate in the presence of a catalyst and the monomer, and then immersed into a solution of $FeCl_3$ in a suitable organic solvent, resulting in coating of the film with a layer of PMT, having a conductivity of 42 S/cm [79].

The enrichment of a surface layer of polymers with an oxidant, followed by exposure to a solution or gas phase, containing monomers, is also often reported as a suitable method of preparing surface-coated conducting composites. Semi-interpenetrating networks of PPy and ethylene-propylene-5-ethylidene-2-norbornene rubber were prepared by two methods [80]. In one of them, rubber was mixed with oxidant $CuCl_2$ and dicumyl peroxide, cross-linked by heating, and exposed to pyrrole vapor. Following the second method, rubber was swollen in $FeCl_3$ solution in tetrahydrofuran, and then exposed to pyrrole vapor. The conductivity of composites prepared following the last method was reported to be higher (10^{-5} S/cm) than that of those prepared by the first (10^{-10} S/cm) [80]. Interpenetrating polymer network composites of PPy and poly(vinyl acetate) (PVA) were prepared by immersing $FeCl_3$-impregnated PVA films into aqueous pyrrole solution [81]. The low values of the percolation threshold for electrical conductivity of the composites prepared, ranging from 3.5 to 5 wt%, have been attributed to fractal growth of PPy phase in the water channels of the swollen films, as supported by SEM images [81]. For PMMA and polycarbonate, no PPy coatings were obtained by this method, since $FeCl_3$ does not penetrate into these materials. Dip-coated poly(ethylene oxide) composite with $CuCl_2$ substrates were coated with PPy by exposing them to the vapor-phase monomer [82]. The conductivity of the films was found to increase with increasing concentration of $CuCl_2$ in the complex, and increasing duration of exposure to pyrrole vapor. The formation of conducting PPy domains in the crystalline regions of the polymer was claimed to proceed during polymerization [82]. Conducting polyacrylamide films were prepared by exposing the polymer films, impregnated with ammonium persulfate, to HCl vapor, and then to aniline vapor [83]. The conductivity of the resulting composite reached 10^{-5} S/cm. Vapor-phase polymerization of pyrrole within the silicon-cross-linked poly(styrene-butyl acrylate-hydroxyethyl acrylate) network using anhydrous $FeCl_3$ as oxidant yielded conductive composite films, having a conductivity up to 15 S/cm [84]. Conducting PPy composite with a secondary cross-linked interpenetrating polymer network was obtained by chemical oxidative polymerization, and the conductivity up to 0.25 S/cm was reported for this composite, having a low content of PPy (0.9 wt%) [85]. The formation of PPy microfiber within the polymer matrix was found by several different techniques [85]. Conducting polymer patterns can be obtained by the dry technique, consisting of an in situ polymerization of the monomer from the vapor phase on a solid oxidizing salt formed on an insulating substrate [86]. Homogeneous, repeatable patterns of polyalkylthiophenes were obtained following this technique, suitable for the implementation of CEP arrays for gas sensing [86].

3.2. Ion-exchange membranes

Ion-exchange resins present useful materials in obtaining CEP composites. Because of their ion-exchange properties, either charged monomers, e.g. aniline in its protonated form, or charged oxidants, e.g. persulfate, or Fe^{3+} ions can be sorbed onto the surface of resins, and then treated with another component needed for polymerization. Some reports on the deposition of CEP onto synthetic ion exchangers relate both to anion and cation exchangers in the form of membranes.

The cation-exchange membrane was charged with aniline by immersion into aniline solution, and then treated with ammonium persulfate, producing a membrane with PANI layers present on both sides, or a membrane with a single PANI layer on one side [87]. These modified composite membranes showed a conductivity up to 5×10^{-3} S/cm, and sodium ion selectivity in electrodialysis, as compared to divalent cations [87]. Cation-exchange membranes were charged with Fe^{3+} ions, and a thin layer of PPy was then deposited in aqueous pyrrole solution [88]. For these membranes, the decrease of permeation of the divalent alkali earth metal cations versus sodium ions was observed, based on the synergistic effect of sieving of divalent cations by a tight and rigid PPy layer [88]. Anion-exchange membranes were coated with PPy by immersing them into pyrrole solution for 24 h, and then into an Fe^{3+}-containing solution, resulting in composite membranes, useful as potentiometric humidity sensors [89]. Anion-exchange membranes were coated with PPy by two different methods: by immersing of membranes, equilibrated in $FeCl_3$ solution, into aqueous pyrrole solution, or, alternatively, by immersing of membranes, equilibrated in pyrrole solution, into aqueous $FeCl_3$ solution, and the resulting composite was found to be homogeneously filled with PPy throughout the membrane in the former case, whereas only surface layers of PPy were found in the latter case [90]. The permeation of the composite membranes in electrodialysis was found to be enhanced for nitrate, but restricted for sulfate [90]. Nafion® membranes were also coated with PPy using $FeCl_3$ as oxidant [91].

3.3. Fibers

Several works have been devoted to the coating of fibers or fibrous materials with CEP. All these works involve a vapor-phase treatment of oxidant-containing carriers with the monomers. Fibrous materials, prepared from polyacrylonitrile and chemically modified polyacrylonitrile which possesses ion-exchange properties, were charged by sorption with $FeCl_3$, provided from aqueous or etheral solution, and then treated with pyrrole vapor, either in vacuum, or from its solution in toluene, yielding PPy-coated composite material [92]. Cotton thread was coated with $FeCl_3$ and exposed to pyrrole vapor, resulting in its coating with a layer of PPy [93]. The resistance of the composite material was found to decrease with increasing concentration of $FeCl_3$ in the thread, and the polymerization temperature. Similarly, cotton thread was saturated with ammonium persulfate, and then exposed to aniline vapor, resulting in its polymerization on the cotton surface [94]. Conducting aramid–PPy composite fibers were obtained by vapor-phase polymerization of pyrrole using $FeCl_3$ oxidant [95]. The resulting composite material showed good thermal stability of conductivity within the range of 170°C. Electrically conductive PPy–poly(*p*-phenylene terephthalamide) composite fibers have been prepared by continuous vapor-phase polymerization using $FeCl_3$ as oxidant [96].

3.4. Glass and inorganics

A glass–polymer composite was obtained by polymerization of aniline, adsorbed in its protonated (i.e. positively charged) form via an ion-exchange process within the pores of Porous Vycor Glass by the use of ammonium persulfate acidic solution as oxidant [97]. As evidenced with Si^{29} NMR spectrometry, SiO^- groups of the glass act in a composite as counter ions for the doping of PANI [97]. CeO_2 coatings were prepared on the glass slides by thermal decomposition of cerium 2-ethylhexanoate, and pyrrole was polymerized onto these slides by the use of the oxidizing ability of Ce(IV), resulting in semiconducting composites [98]. A layer of MnO_2 was electrodeposited on platinum, and used as oxidant in the polymerization of aniline on it [99]. A serious problem in obtaining CEP coatings onto a smooth glass surface is the poor adhesion of the polymer layer to the glass substrate. To improve adhesion, glass fibers were treated with new pyrrole-substituted organotrialkoxysilanes, and a vapor deposition of PPy was performed onto this modified glass surface, resulting in unusual high electric conductivity of the PPy coating of

150–200 S/cm, which can be related to the high regularity of the deposit [100]. Morphological investigations of PPy thin coatings onto glass, silicon and silicon dioxide substrates, coated with an oxidizing precursor, and obtained by vapor polymerization, showed that variation of the deposition parameters results in the control of the film microstructure, which can be fibrillar and strongly anisotropic, or globular and tendentially isotropic [101]. Multilayer xerogel–PPy composites were prepared by alternate successive treatments of glass with a siloxane functionalized pyrrole, oxidant, and a sol precursor for the xerogel [102]. Different metal oxide particles (α-Fe_2O_3, CeO_2, CuO, NiO, and SiO_2) were coated with PPy by reacting the dispersed particles in water–ethanol mixture with pyrrole without the use of additional oxidant [103]. It was found that only CeO_2 and CuO promoted polymerization in the absence of oxygen, whereas all materials used were successfully coated in the presence of oxygen [103].

3.5. Miscellaneous

Inverted emulsion polymerization was employed to prepare CEP-containing composites. The solution of aniline in organic solvent was introduced into an inverted emulsion, containing an organic solution of a host polymer and a dispersant as a continuous phase, and an aqueous solution as a dispersed phase, and after the completion of polymerization, a composite was obtained by precipitation of PANI together with a host polymer [104]. In a modification of this method, an aqueous solution of the oxidant is introduced into an inverted emulsion, containing aniline in an organic phase [104]. The conductivity of the composites prepared are reported to be 0.35–0.48 S/cm, and 1.0–2.8 S/cm for the first and second methods used, respectively [104]. Following a similar method, PMT composites with rubber were prepared, having a conductivity of 1.3 S/cm, and an elongation of 84% at the break point [105].

Pyrrole was grafted onto a PMMA backbone which contained the pyrrole moiety, via oxidative polymerization with $FeCl_3$ in nitromethane, and a maximum conductivity of 10^{-2} was obtained for this composite [106]. PPy–PVC composite films were prepared by the modification of the diffusion-oxidative polymerization, i.e. PVC was dissolved in tetrahydrofuran together with pyrrole, the resulting solution was cast in Petri dishes, and the obtained strips were dipped into an aqueous solution of $FeCl_3$ [107]. Thin PPy films were obtained on the poly(ethylene oxide)–$FeCl_3$ (7:3) coordination complex, and the resulting composite was used to obtain thin films on human teeth [108]. PPy films with a thickness of 3–4 μm were prepared by chemical oxidation of pyrrole at the interface of chloroform and water with ammonium persulfate as oxidant [109]. The films were reported to be compact and could be removed with a solid plate [109]. Animal tissue porcine pericardium was impregnated with pyrrole or its derivative sodium 4-(3-pyrrolyl)butanesulfonate, by soaking the tissue in the monomer, and then treating it with $FeCl_3$ solution, producing black PPy-tissue hybrid biomaterial [110].

4. Deposition of CEP on micro- and nanostructured materials

Both bulk and surface polymerization have been reported in a number of publications to cover various small structures like micro- and nanoparticles, or microporous materials. According to the nature of materials involved in obtaining microcomposites, the material reviewed is divided below into a few groups, dealing with diverse inorganic and organic materials.

4.1. Elements

Silicon, carbon and gold microstructures were reported to be coated with CEP, yielding new composites. The n(+)-type porous silicon was covered with PANI by chemical oxidative polymerization [111]. The polymerization proceeded inside the Si pores, and the pores were found to be totally filled after the deposition of five layers of PANI [111]. A light-emitting diode was reported on basis of n(+)-type porous silicon with tight filling of the pores by PANI [112]. The diode showed rectifying I–V characteristics, and emitted red light under a forward bias voltage exceeding 3 V [112].

Hollow nanoscopic PPy and poly(*N*-methylpyrrole) capsules were synthesized on the gold nanoparticles as templates for polymer growth [113]. Chemical etching of the gold leaves a structurally intact hollow polymer capsule with a shell thickness of 5 to more than 100 nm, and a hollow core diameter of 5–200 nm [113].

The composites of PPy and carbon black were prepared by chemical polymerization of pyrrole in an aqueous dispersion of carbon black [114]. The application of these composites in an environmental remediation was proposed, and demonstrated for Cr(VI) as a model pollutant [114]. A new type of carbon nanotube with a diameter of 100 nm was obtained by in situ polymerization of pyrrole on nanotubes [115].

4.2. Metal oxides

Chemical polymerization of pyrrole was provided in the presence of various ultrafine dispersed inorganic oxide sols such as tin(IV) oxide, zirconia, antimony(V) oxide, yttria, and titanium(IV) oxide [116]. Only tin(IV) oxide sols acted as effective particulate dispersants, whereas other oxides studied failed to prevent macroscopic precipitation of the PPy. The highest conductivity for PPy–SnO_2 nanocomposites was found to be 23 S/cm [116]. Ultrafine tin(IV) oxide particles were used as a particulate dispersant for PPy in its chemical synthesis, and the resulting PPy–SnO_2 nanocomposite had a conductivity up to 4 S/cm [117,118].

Uniform spherical colloidal copper oxide particles were coated with PANI in the mixture containing CuO, aniline, and PVA without the oxidant added [119]. The resulting dispersion, besides CuO with a polymer shell, contained also independent PANI (latex) particles. Oxygen was found to be essential for this synthesis, acting as a promoter for the polymerization, while PVA formed micelles that enhance the reaction rate and protect PANI from hydrolysis [119]. At a reaction temperature of 90°C, a coating of more than 10 wt% was achieved in 48 h [119]. Aniline was intercalated into a layer-structured host material MoO_3 by the treatment of sodium ion-intercalated MoO_3 with a mixture of neutral aniline and anilinium ions, and the polymerization of intercalated aniline was performed by direct reaction with an oxidizing agent in aqueous solution, and then by exposing the dried material to an oxidizing vapor [120].

Composite powders of PPy and either α-MnO_2, β-MnO_2, or spinel $LiMn_2O_4$ were prepared by injecting liquid pyrrole into an acidic medium containing suspended MnO_2 powder, acting as oxidizing agent [121]. The resulting composites were tested as cathode materials for rechargeable lithium batteries, and it was shown that PPy acted well both as an active material and as a conducting network for manganese dioxide [121]. Layered oxides $HMWO_6 \cdot nH_2O$ (where M = Ta, Nb) were used to intercalate aniline, forming a bilayer of the guest species, and the thermal treatment in air that followed resulted in a polymerization of a part of aniline, and the formation of a new nanocomposite $PANI_{0.34}HMWO_6$ [122]. The resulting material was used as cathode material in conventional lithium cells [122]. Similarly, aniline was intercalated into $HMMoO_6$ (M = Ta, Nb), possessing a rutile-like structure, and oxidized by heating in air at 130°C, yielding a new nanocomposite material [123].

PANI was synthesized in $V_2O_5 \cdot nH_2O$ xerogel by in situ intercalation and polymerization of aniline or its salt, and a monolayer of PANI was concluded to be present in the V_2O_5 framework, based on the interlayer separation of 0.56 nm [124]. The crucial role of oxygen in this process was pointed out, and it was shown that oxygen can act as an electron acceptor both during the in situ reaction, and after intercalation is complete. The conductivity of the freshly prepared composite was in the range 10^{-4}–10^{-1} S/cm depending on the degree of polymerization, but the conductivity of aged composites was a little higher [124]. V_2O_5–PPy aerogel composites have been synthesized by the sol–gel procedure, following simultaneous polymerization of pyrrole and vanadium alkoxide precursors by hydrolysis of $VO(OC_3H_7)_3$ using pyrrole–water–acetone mixtures [125]. The addition of ammonium persulfate as an oxidizing agent increased the conductivity of the material.

Fine grade powder (particle size ca. 100 nm) of anatase TiO_2 was used in the polymerization mixture, and a PANI–TiO_2 composite was obtained [126]. A much higher yield of PANI was found to be formed in the presence of TiO_2 particles, than without TiO_2 added. The composites obtained exhibited high piezoresistivity with piezosensitivity having a maximum value at a definite composition of a composite [126]. The composite of PANI with iron oxides of nanometer size was prepared by chemical polymerization [127]. Pyrrole was polymerized in the presence of ultrafine zirconium(IV) oxide particles which act as a dispersant for pyrrole [128]. It was found that the conductivity of the nanocomposite was higher than that of PPy, prepared in the absence of ZrO_2, and increased with ZrO_2 concentration up to a certain limit [128]. Polymerization of CEP onto different oxides, as well as other inorganic host materials, was reviewed recently [129].

4.3. Silica

Numerous papers describe the deposition of PANI, PPy, or their derivatives on micro- and nanometer-sized silica particles. Aniline was chemically polymerized in the presence of ultrafine colloidal silica particles with a diameter of 35 nm, and colloidally stable PANI–silica particles were obtained [130]. The particles obtained had a diameter ranging from 300 to 600 nm, and electric conductivity of 6.1×10^{-2} S/cm for the composite, containing 37.8 wt% of silica [130]. Besides PANI, poly(*o*-anisidine) coated silica particles were obtained by chemical polymerization using ammonium persulfate in the presence of silica particles [131]. A faster polymerization reaction of aniline using sodium persulfate and potassium iodate as oxidants was reported to proceed in the presence of ultrafine 20 nm silica particles to form PANI–silica colloidal composites, as compared to the same reaction performed without the addition of silica [132]. Both the isoelectric points and zeta potentials of PANI–silica and PPy–silica, prepared by chemical polymerization in the presence of commercially available silica particles, were found to be governed primarily by the nature of the charged groups of silica surface rather than by the CEP component [133]. This suggests that silica is a major component at the particle surface, which is consistent with the good long-term colloidal stability of these composites [133]. It was confirmed by XPS spectroscopy that the surface composition of CEP–silica colloidal nanoparticles is silica-rich with respect to their bulk composition [134].

Because of the silica-rich surface of CEP–silica composites, a low electric conductivity is observed for these materials, when compressed e.g. into pellets. In order to enrich the surface of nanocomposites with CEP, silica gel particles were pretreated with a silane coupling agent aminopropyltriethoxysilane (APS), followed by chemical polymerization of pyrrole, resulting in higher PPy loading, higher specific surface area with a PPy-rich surface, and a much greater conductivity (by ca. 3 orders of magnitude) [135]. In absence of the APS pretreatment, PPy is loaded mainly in the pores of silica gel, resulting in a poor conductivity, whereas APS pretreatment results in a substantial increase in PPy mass loading (from 6 to 11.5 wt%), and much higher conductivity [136]. A thin overlayer of PPy on silica particles was obtained after the APS pretreatment, whereas a predominant polymerization within the pores was reported for the non-treated silica gel [137]. The surface area of APS pretreated silica–PPy nanocomposite (162–184 m^2/g) was found to be significantly lower than that of the non-pretreated composite (422 m^2/g), or of native silica gel (431 m^2/g) [137]. The state of the surface for PPy–silica nanocomposites was reported to depend upon the oxidant used in polymerization, e.g. silica-rich and colloidally stable composites were obtained by the use of ammonium persulfate as oxidant, whereas PPy-rich and less colloidally stable composites were obtained using $FeCl_3$ [138]. The morphology of PPy–silica composites was also reported to depend upon the oxidant used in polymerization [139]. Stable colloidal dispersions were prepared by copolymerization of pyrrole and 1-(2-carboxyethyl)pyrrole in the presence of silica particles [140]. Copolymers of pyrrole and pyrrole-3-acetic acid were prepared on silica by chemical copolymerization with the use of hydrogen peroxide, and it was shown that by increasing the proportion of pyrrole-3-acetic acid in the comonomer feed, a higher degree of surface carboxylation was obtained [141]. Colloidal PPy–magnetite–silica nanocomposites were prepared by first deposition of silica onto ultrafine (5–20 nm) magnetite particles via controlled hydrolysis of sodium silicate, and the following chemical polymerization of pyrrole with various oxidants in the presence of these particles [142].

4.4. Diverse inorganic materials

Besides oxides, some other inorganic materials were involved in obtaining CEP-containing nanocomposites. Two approaches were reported for the preparation of PANI-containing nanocomposite with α-$Sn(HPO_4)_2{\cdot}2H_2O$ [143]. First, the inorganic material was charged with Fe^{3+} ions, and then used in oxidative polymerization of aniline, proceeding inside the layers of inorganic material, or, secondly, aniline was intercalated in the material, and polymerization was performed by ammonium persulfate solution [143]. Similarly, Sn(IV) 2-carboxyethyl phosphonate was charged with Fe^{3+} ions by ion-exchange process, and then PANI was chemically synthesized in the interlayer space of the host matrix, resulting in PANI content of up to 3.5 wt% in the resulting composite [144]. Zirconium phosphate sulfophenylphosphonate was employed as a template for aniline because of the presence of strongly hydrophilic sulfogroups, and the resulting molecular complex can be polymerized to PANI [145]. Metal phosphonates α-$Ti(HOPO_3){\cdot}H_2O$, α-$Zr(HOPO_3)_2{\cdot}H_2O$, and $HUO_2PO_4{\cdot}4H_2O$ were used for intercalation of aniline and *N*-phenyl-*p*-phenylenediamine, and, after thermal treatment at 130°C in air, intercalated aniline and its derivative are slowly polymerized by ambient oxygen [146]. Following polymerization, the interlayer spacing increases slightly from 10.46 to 11.8 Å for anilinium/uranyl phosphate, but decreases greatly from 28.3 to 20.5 Å for zirconium phosphate, and from 18.87 to 13.25 Å for titanium phosphate, indicating a monolayer of PANI inside the uranyl and titanium phosphates, but a bilayer in zirconium phosphate [146]. Polymerization of 4-anilinoaniline (aniline dimer) in the powdered $VOPO_4$ and V_2O_5 interlayer spaces was also reported [147].

The direct intercalative encapsulation of PPy into MoS_2 was performed by the oxidation of aqueous pyrrole solution in the presence of single MoS_2 layers [148]. The resulting nanocomposite showed an interlayer expansion of 4.5 Å, consistent with a monolayer of PPy in the gallery space of the host matrix [148]. PANI–MoS_3 composite was prepared by chemical polymerization in aqueous solution, containing aniline and ammonium tetrathiomolybdate [149]. Conducting PANI–$BaTiO_3$ composites have been prepared by placing the fine grade powder of barium titanate in the polymerization reaction mixture [150]. Conducting PANI–$BaSO_4$ composite particles of 10–20 nm diameter have been synthesized in inverse microemulsions, and the conductivity of the resulting composite was found to range from 0.017 to 5 S/cm with increase of PANI content from 5 to 22 wt% [151]. α-$RuCl_3$ was proposed as a host matrix for the in situ redox intercalative polymerization of aniline [152].

4.5. Clays and zeolites

Many clay materials can be ion exchanged or impregnated with positively charged metal cations, and some of these cations, like Fe^{3+} and Cu^{2+}, can promote the chemical polymerization leading to coating of these minerals with CEP. PPy–montmorillonite nanocomposites have been prepared by the polymerization of pyrrole at $FeCl_3$-impregnated montmorillonite [153]. X-ray diffraction study showed no change in interlamellar spacing of the mineral, suggesting no intercalation of PPy into lamellae. The bulk conductivity of the composites varied around 10^{-5}–10^{-4} S/cm, depending on the $FeCl_3$ impregnation level and on the PPy loading [153]. Conducting PPy–montmorillonite composite is formed at the ferric sites present at the accessible surfaces of the clay particles, as evidenced by in situ FTIR-ATR spectroscopy [154]. *N*-vinylcarbazole was also polymerized on $FeCl_3$-impregnated montmorillonite [155].

The inclusion of aniline into Cu^{2+} exchanged hectorite thin films is followed by the subsequent polymerization on the clay surface and in the intergallery regions [156]. The nearly two-dimensional polymer sheets have been found to form in the intergallery regions. The composite materials prepared have been pointed out to be suitable as chemical sensors for some gases and vapors such as ethanol and hexane [156]. PANI–hectorite and PANI–montmorillonite composite materials have been prepared by exposing Cu^{2+} exchanged silicate materials to aniline vapor, and the resulting materials have been claimed to be useful as chemical sensors [157]. Aniline vapor is spontaneously polymerized on the surface of Cu^{2+} exchanged hectorite due to micropore sites on the silicate surface where oxidizing Cu^{2+} cations are available [158]. Cu^{2+} exchanged hectorite films, exposed to aniline at room temperature, revealed a post-polymerization structure on the hectorite surface consisting of small PANI bundles with a diameter of 300–3000 Å, similar to the structure observed on electropolymerized PANI films [159]. When polymerized at 180°C, PANI revealed a structure similar to undoped solution-cast PANI film [159].

Polymerization of pyrrole was performed in the tunnels of sepiolite adsorbing J_2 to obtain a linear polymer in the limited space of a tunnel, and composites of PPy and sepiolite were obtained [160]. Colloidal composite nanoparticles were also prepared by the interaction of colloidal PPy and PT with the colloidal, exfoliated host montmorillonite [161].

Rutile-type $HNbMoO_6$ was intercalated with aniline, and subsequent polymerization was performed using $FeCl_3$, resulting in a composite material $(PANI)_yNbMoO_6$, where y ranges from 0.26 to 0.64 [162]. Layered perovskites $HCa_2Nb_3O_{10}$ and $HCa_2Nb_2MO_9$ ($M = Al$, Fe) were intercalated with aniline, and subsequently treated with ammonium persulfate, yielding PANI-layered perovskite composites [163]. It was shown that PANI exists within the galleries of the host matrix in emeraldine form [163]. PPy composites with two kinds of zeolite (NaY and USY) were prepared by the gas diffusion process, provided for Cu^{2+} enriched host material [164]. The inclusion chemistry of CEP in inorganic hosts, mostly zeolites, was reviewed [165]. Ceramic–PANI composite porous membranes were prepared by diffusing ammonium persulfate and aniline into inorganic membrane disks [166].

4.6. Glass

CEP–glass nanocomposites were obtained by in situ polymerization of pyrrole and aniline inside the pores of porous glass via Cu^{2+} impregnated in the glass pores, and using ammonium persulfate as oxidant [167]. Porous glass having pores of a diameter of 20–200 Å, was enriched with Cu^{2+} ions, and polymerization of pyrrole was performed in the glass pores, yielding glass-encapsulated molecular wires [168]. In situ polymerization of pyrrole was provided on the Cu^{2+} exchanged porous surface of $LiTi_2(PO_4)_3$ glass ceramic [169].

4.7. Organic materials

Considerable interest has been paid to micro- and nanostructured CEP, obtained within the pores of membranes. Nanocomposites of PPy were obtained by chemical polymerization within the pores of microporous and nanoporous particle track-etched membranes [170]. Since PPy deposits initially on the inner walls of the pores, hollow tubes of PPy can be formed, whereas PPy wires (filled tubules) were obtained by repeating polymerization a few times [170]. Nanotubules and nanofibrils of PPy have been synthesized within the pores of nanoporous polycarbonate membrane filters as templates [171]. It was shown that template-synthesized nanofibrils of PPy have an enhanced conductivity, and that this enhancement is critically dependent on the diameter of the nanofibrils in such a way that the fibrils of the narrowest diameter show the greatest enhancement in conductivity [171]. Perfectly cylindrical PPy tubules of 15 nm diameter were obtained by chemical polymerization of pyrrole within nanoporous particle track-etched polycarbonate membranes [172]. PPy microtubules have been synthesized within the pores of a polycarbonate template, and a glucose biosensor has been fabricated by the electrochemical adsorption of glucose oxidase on the PPy nanotubular layer [173]. PPy was synthesized by oxidative gas-phase polymerization on the microporous polyethylene film [174,175]. Different CEP have been synthesized within the pores of microfiltration membranes, containing linear, cylindrical pores with a diameter ranging from 10 nm to 10 μm, and it has been shown that, for the narrowest pores, the concentration of radicals formed during polymerization is low compared to the concentration of monomers, resulting in a material with higher conductivity [176]. PPy microtubules with a diameter of 400 nm have been synthesized in the host membrane, and it has been shown that the microtubules are not homogeneous, but are composed of layers with different electrical conductivity [177].

The deposition of thin CEP layers onto micro- and nano-sized polymer suspensions or latexes have also attracted considerable interest. PANI overlayers have been synthesized onto micrometer-sized poly(*N*-vinylpyrrolidone) stabilized latexes under various synthesis conditions [178]. It has been found that PANI coatings are much less uniform than the PPy overlayers, and that the uniformity can be improved using aniline hydrochloride in the absence of HCl for the polymerization procedure [178]. Similarly, PPy layers were deposited onto poly(*N*-vinylpyrrolidone) stabilized polystyrene latex particles, leading to composites having an anomalously low percolation threshold of conductivity of 1–2 vol%, as measured for the pressed pellets of dried material [179]. Poly(*N*-vinylpyrrolidone) stabilized polystyrene latex has been coated with poly(3,4-ethylenedioxythiophene) (PEDOT) in aqueous solution using Fe(III) tris(*p*-toluenesulfonate) complex as oxidant, and a series of PEDOT-coated latexes as obtained with PEDOT loadings varying from 4.9 to 38.0 wt%, characterized by a percolation threshold of ca. 5 vol% and a conductivity of 0.43 S/cm [180]. Micrometer-sized PPy-coated polystyrene latexes have smooth and uniform surface at low PPy loadings (1 wt%), but a rough, more globular morphology was observed for composite latexes having higher PPy loadings (8.9 wt%) [181]. For these composite latexes, the underlying latex core was quantitatively removed by the solvent extraction procedure, leaving PPy residues of a “broken egg shell” morphology [181]. PANI–poly(butadiene-*co*-styrene-*co*-2-vinylpyridine) latex composites were prepared by aniline polymerization in the presence of latex, and mass loading of PANI in the composite latex was controlled by varying the latex/aniline charging ratio, and oxidant/aniline molar ratio [182]. PANI and PPy colloidal compositions were prepared with commercial aqueous resin dispersions, stabilized by non-ionic surfactants, and core-shell particles were shown to exist in PPy/polyurethane and PPy/alkyd dispersions [183]. Porous PMMA particles with different specific surface area were prepared by seeded emulsion polymerization, and the incorporation of PPy into porous particles was achieved by chemical oxidative polymerization [184]. Micrometer-sized, sterically stabilized polystyrene latex particles were coated with an outer layer of PPy in order to improve the processability of PPy [185].

5. Concluding remarks

The material reviewed reflects a wide spectrum of the investigation done on the coating of different materials with layers of CEP. Numerous methods of coating were elaborated, and a wide variety of materials were coated with different CEP. It seems that, at least in principle, nearly all kinds of materials can be coated with CEP, yielding new composite materials that can be used in various fields such as in the metallization of dielectric materials, in the preparation of radar absorbing materials [186], microwave obscurants [187], or in chemical sensors [188,189].

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