POLYPYRROLE AND POLYPYRROLE/WOOD-DERIVED MATERIALS CONDUCTING COMPOSITES: A REVIEW

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Wood and cellulose derivatives, in both fibrous and water-soluble macromolecular form, are emerging as outstanding candidates for organic electronics applications due to their large-scale availability, low cost, and easy processability. Paper and wood fibre-based derivatives are considered to be materials of choice as supports for communication world-wide. The interest in producing inexpensive and universally available conducting polymer/cellulose fibres substrates resides in the possibility of creating new materials that can be used for a broad range of advanced applications. For instance, PPy/cellulose fibres composites can be used for the preparation of energy storage devices thanks to the conjugation of the high specific area of cellulose fibres and the electrochemical properties of PPy. Other possible applications of such composites are in the area of the antistatic materials, sensors, electromagnetic interference shielding materials, smart packaging, and tissues. Concerning the woody polymers, some of them (i.e. cellulose derivatives) also exhibit biocompatibility, as well as film-forming properties and transparency. In combination with the electrical properties of PPy, these features make PPy/macromolecular cellulose composites suitable for applications as displays, lighting, and photovoltaics. Due to their chemical structure, macromolecular wood derivatives have been proposed with success as enhancing conductivity additives in Py polymerisation. The aim of the present review is to provide an overview of PPy chemistry and of the most relevant advances attained in the production of PPy/wood derived materials conducting composites.

POLYPYRROLE

The aqueous synthesis of polypyrrole as an insoluble black precipitate, formerly known as pyrrole black, from an acidic pyrrole/H_2O_2 solution, was documented for the first time by Angeli (1916). However, PPy semiconducting properties have been highlighted only in the pioneering works of McNeil et al. (1963) and Dall'Olio et al. (1968) who synthesised PPy by the pyrolisis of tetraiodopyrrole and electrolytic oxidation of pyrrole in a H_2SO_4 solution, respectively. At first, the electrochemical synthesis, as well as the ability to obtain highly conducting PPy films, triggered an enormous

interest (Diaz et al. 1979, 1981; Kanazawa et al. 1981; Genies et al. 1983) and the cationic radical synthesis in water or organic solvents was disregarded, owing to the insolubility of PPy precipitates and their low processability (Angeli 1916; Salmon et al. 1982). More recently, the use of anionic surfactants during pyrrole chemical polymerisation (Lee et al. 1995, 1997; Oh et al. 2002) made it possible to obtain soluble polypyrrole that can be easily used for casting conducting PPy films. These works demonstrated that soluble and water dispersible PPy can be obtained by chemical polymerization, thus opening the way to a new broad range of applications. For this reason, the latest literature on the elaboration and use of chemically synthesised PPy is very abundant. In order to match with the aim of this review and to provide a background for the comprehension of PPy/wood derived materials elaboration, this section focuses only on fundamental aspects related to PPy aqueous chemical synthesis.

Aqueous Phase Py polymerisation

Polymerisation mechanism

Polypyrrole can be obtained mainly through cationic radical, electrochemical, or vapour-phase polymerisation. Among these methods, the cationic radical synthesis is the only way allowing the production of high quantity massive conducting polymer and the most promising for industrial applications.

Py polymerisation occurs through the oxidation of the monomer, *via* a pseudo-polycondensation mechanism (Fig. 1) (Planche et al. 1994; Reinisch et al. 1979).
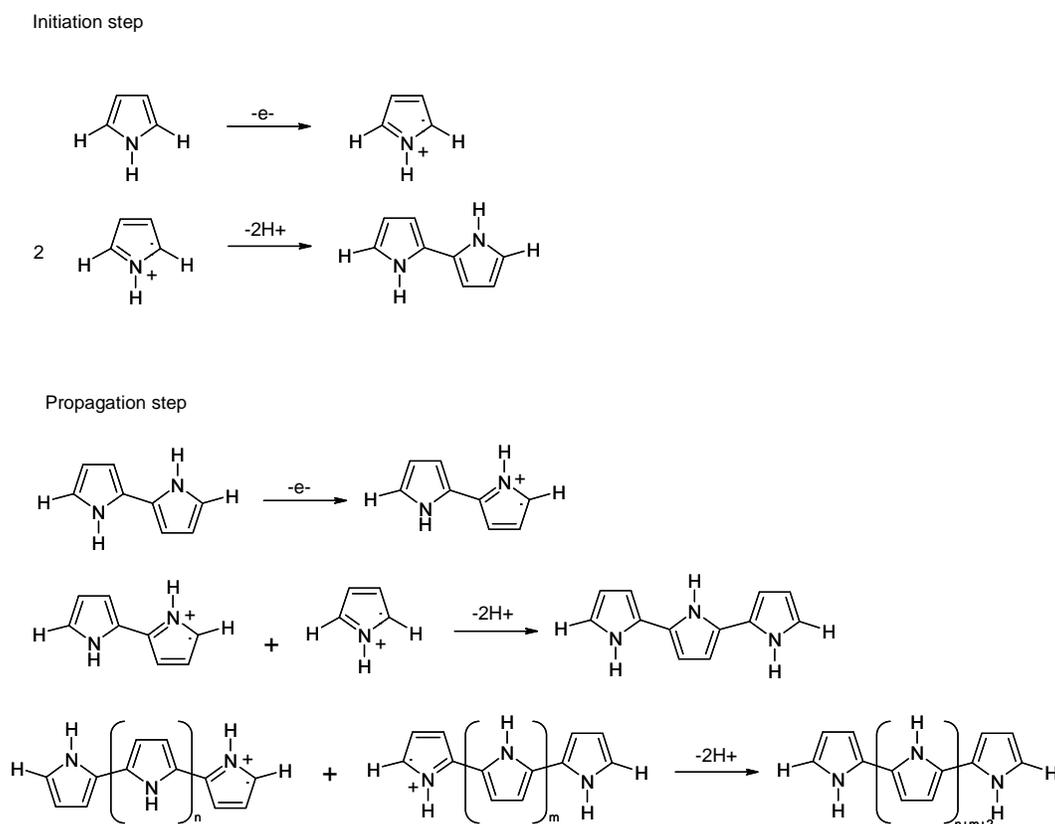

Fig. 1. Pyrrole polymerisation mechanism

In the initiation step, monomers are oxidised and radical cations are formed. Then, these radical species couple through deprotonation, forming soluble bipyrroles.

Then, in the propagation step, bipyrroles are oxidised again, and oligomers with radical cations are produced. The further coupling of these species leads to the formation of higher oligomers and of an extended conjugated polymer (Skotheim and Reynolds 2007). Owing to the solubility of Py oligomers with polymerization degree $DP_n < 30$ (Appel et al. 1999), polymerisation starts in the continuous liquid phase and, when Py oligomers are no longer soluble, solid PPy clusters form in the polymerisation medium. The polymerisation will continue mainly at the surface or inside the solid polymer particles, depending on the activation of surface sites and on the diffusion of the reactive species within the formed polymer. In this case, diffusion deals with the movement of the initiator toward the monomer (and *vice-versa*) but also with the self-diffusion of the monomer towards the system (solvent, monomer, polymer,…).

Polymerisation kinetics

The kinetics of Py aqueous cationic radical polymerisation depends on the oxidant, the monomer/oxidant ratio, and the temperature. For short-time polymerisation, i.e. less than 1 hour (or mild oxidants), it is generally found that the reaction follows pseudo-first-order kinetics, i.e. $[Py] = [Py]_0 e^{-kt}$, where [Py] is the monomer concentration at time t, $[Py]_0$ is the initial Py concentration, and k is the kinetic rate constant (Ferrero et al. 2006; Planche et al. 1994; Cavallaro 1999; Stankovic et al. 1995).

Even though long (up to 12-24 hours) polymerisation times have often been applied (Song et al 2004; Oh et al. 2001; Lee et al. 2000), the kinetics of such systems have been poorly analysed in the literature. The principal reason is that the complex reaction mechanism of PPy is not yet fully understood. This is even more of an issue for long polymerisation times, during which different side reactions can occur. The complexity in determining long-time pyrrole polymerisation rates derives principally from the polyphasic system and the difficulty in evaluating Py functionality.

During polymerisation, different species can act as oxidants, in addition to the oxidising agent voluntary introduced for the polymerisation. It was reported by Novak (1992) that during aqueous polymerization, PPy chains can be oxidised by OH⁻ ions, and also they can undergo some direct reactions with oxygen. Other species, deriving mainly from the dissociation of the principal oxidant (as HSO_4^- for ammonium peroxodisulfate, APS), are supposed to attack the monomers (Blinova et al. 2007). This is particularly true for long polymerisation times.

Moreover, pyrrole polymerisation does not proceed linearly. At the beginning of the polymerisation, the electrical charge within the pyrrole ring allows linear α-α' linkages to form, leading to linear molecules. With the polymer growth, the monomer charge is differently distributed in the ring, thus allowing the activation of β' sites. So α-β' linkages between the growing chains are created, and the molecules can develop three-dimensional structures. Moreover, to counterbalance the charge, the added monomers (or chains) can have different inclinations, giving rise to distorted arrangements, such as cones or helices (Schmeisser et al. 1993; Appel et al. 1999; Naarmann et al. 1998). These facts render the functionality of the pyrrole ring and the polymerisation degree of the final polymer difficult to estimate, which, as schematized in Fig. 2, is reflected by the

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generation of insoluble cross-linked structures with reduced conjugation length and electron conductivity. Few data on PPy molecular weight (Oh et al. 2001) indicate that in the presence of a conductivity enhancer and a long polymerisation time, i.e. di(2-ethylhexyl) sulfoccinate and 20 h, respectively, a DP_n of 303 can be attained. Other studies (Lee et al. 1995; Song et al. 2000) did not succeed in estimating the DP_n of PPy synthesised in the presence of dodecylbenzenesulfonic acid and concluded that PPy was composed mainly by high oligomers with a degree of polymerisation too low to be detected by viscosity and dynamic light scattering measurements.

Factors affecting pyrrole polymerisation

An oxidising agent is a chemical compound capable of withdrawing electrons. It must enable the polymerisation initiation and propagation. Typical oxidants for Py polymerisation are metal transition salts (Chao and March 1998), halogens (Neoh et al. 1989, Kang et al. 1986), and persulfates (Khulbe et al. 1982; Malinauskas 2001). Depending on its oxido-reduction potential, the oxidant affects the polymerisation kinetics and consequently PPy conductivity and morphology (Xing and Zhao 2007). Among the oxidants, iron chloride ($FeCl_3$), and ammonium peroxodisulfate (APS, $(NH_4)_2S_2O_8$), are two of the most widely studied. Generally, the former, having a redox potential lower then the latter (persulfate: 2.01 eV; Fe(III): 0.77 eV, both in standard conditions), induces slower and more controlled reactions (Xing and Zhao 2007; Mandal and Mandal 1999).

The oxidant performance in terms of PPy final conductivity depends strictly on the Py/oxidant ratio (Armes et al. 1987). An excess of oxidant is necessary to guarantee the electron withdrawal from Py, but this excess must not be higher than a certain level in order to avoid degradation of PPy chains (over-oxidation).
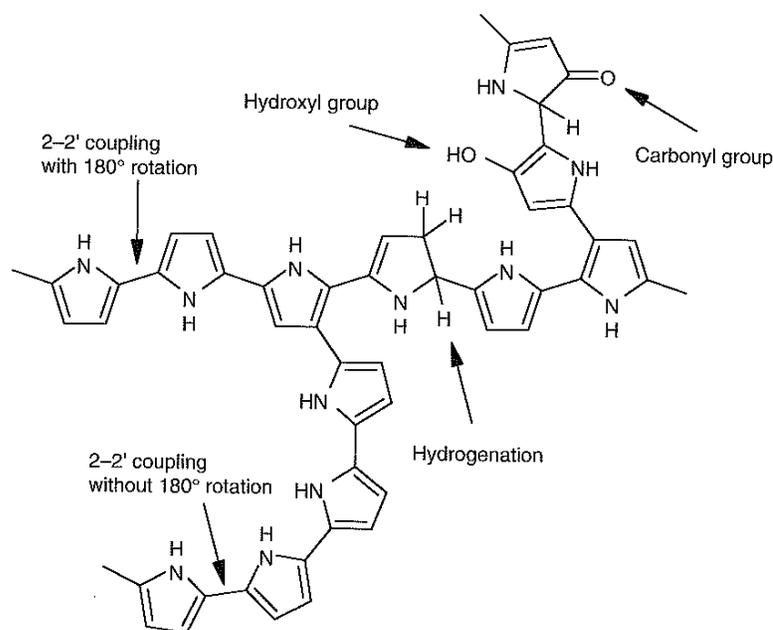

Fig. 2. Schematic representation of reticulated PPy and possible chemical and conformational defects

In chemical synthesis, the doping process occurs simultaneously with the chain oxidation. In fact, the decomposition of the oxidant, particularly with salt-like oxidants, frequently gives rise to ions that act as dopant. In the case of $FeCl_3$ and APS, the dopants are chloride (Cl^-, ClO_4^-,...) and sulfate (SO_4^-) derivative ions, respectively (Beneventi et al. 2006; Blinova et al. 2007).

It was recently shown that the use of macromolecules in PPy synthesis led to an improvement in the polymer conductivity. These macromolecules are co-dopants, or additives (normally called dopants), and they induce also morphological/chemical modification of the polymer (see the conductivity enhancers section).

Determining the optimal polymerisation time means controlling the balance between the development of conjugated system (which length is associated with the conductivity), and its over-oxidation (i.e. the disruption of conjugation) (Novak 1992; Thieblemont et al. 1994; Dall'Acqua 2004). In fact, it was found that by modifying only the polymerisation time, orders of magnitude variations in conductivity were detected. Indeed, the importance of polymerisation time in obtaining highly conducting PPy is correlated to the electrochemistry of the oxidant. Oxidants with high redox potential would quickly oxidise Py, but they also rapidly degrade the newly formed PPy chains and promote PPy interchains cross-linking. In this case, time can greatly affect PPy conductivity. By contrast, the use of less aggressive oxidants makes time a secondary parameter.

It is usually accepted that the best PPy conductivities are obtained with lower temperatures (Fig. 3) (Lee et al. 1997). Temperature influences both the polymerisation kinetics (consequently the regular polymer development), and the number of side reactions (Kudoh et al. 1998). At low temperature, the kinetics are slowed down, and a quite linear PPy is obtained. The charge carrier movement, in this case, is favoured due to the regularity of conjugation.
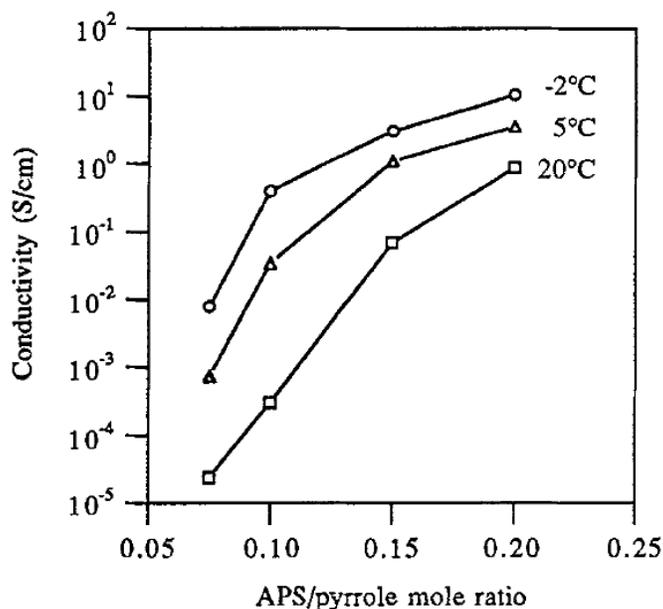

Fig. 3. Temperature impact on PPy pellets conductivity. Reprinted with permission from (Lee et al. 1997). Copyright 1997, Elsevier

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By contrast, when temperature is increased, the kinetics are accelerated. In this case, many sites in the Py ring are activated, leading to extensive PPy cross-linking and to a three-dimensional polymer growth. In such an irregular structure, charge mobility is impeded. With temperature, the number of side reactions (between oxidant species present in the polymerisation reactor and the PPy chains) increases, thus inducing the possibility of interruption of conjugation (Kassim et al. 2002).

Conductivity enhancers.

Additives can be used during Py polymerisation with the aim of providing specific properties to the polymer. These additives, usually surfactants or polymeric stabilizers, can improve PPy conductivity, thermal and air stability, polymerisation yield, and PPy particles morphology.

The efficiency of an additive in enhancing conductivity is strictly associated with its chemical/electrochemical characteristics. Anionic additives display better performances than their cationic or non-ionic homologues (Omastova et al. 1998; Shen and Wan 1998, Zhang et al. 2006). This can be attributed to the fact that negatively charged molecules interact with PPy by counterbalancing their positive charge and remain trapped within PPy clusters. Moreover, they act as counterions (as dopants), thus supplying an additional doping action and improving the conductivity. On the other hand, cationic and non-ionic additives, due to their positive or null charge, have repulsive and weak attractive ion-dipole interactions and do not act as PPy counterions. Therefore, the final electrical properties of PPy are not altered. Among the anionic additives, alkyl sulfonates, particularly alkyl benzene sulfonates, are the most effective additives in term of conductivity improvement (Shen and Wan 1998; Kudoh 1996; Oh et al. 2001). PPy pellets with conductivity up to 100 S/cm have been obtained by synthesising the polymer with APS and toluenesulfonic or butylbenzenesulfonic acids (Song et al. 2004).

It was demonstrated that molecular weight and steric hindrance affect the additive's electroactivity towards PPy (Shen and Wan 1998). Additives with lower molecular weight (or shorter alkyl chain length) can diffuse more easily in the medium, thus well approaching the growing PPy chains and counterbalancing the polymer charge. Moreover, with a minor steric hindrance, they allow PPy short range order arrangement, thus resulting in an elevated final conductivity (Song et al. 2004).

A positive contribution to conductivity will be noticed until a certain additive concentration, before the tendency is inversed. In fact, for each system an optimal concentration leading to a maximum in conductivity can be found. Beyond this value, the system becomes overcharged and the presence of non-conducting elements hinders the conductivity: PPy is thus over-oxidised and degraded, and the additive hindrance towards PPy impedes the charges movement (Omastova et al. 2004).

Being incorporated to PPy, additives induce an increase of the polymerisation yield. Moreover, anionic additives (i.e. aromatic sulfonates or benzene sulfonate surfactants) are permanently incorporated into PPy, and their hydrophobic moieties protect PPy-additive ionic bonds with a subsequent improvement of PPy thermooxidative and moisture stability (Kudoh 1996, Omastova et al. 2003, Ansari 2006) . In Table 1 the most frequently used additives with relative PPy pellets conductivity are reported.

Table 1. The Most Widely Used Additives and Relative PPy Pellets Conductivity

Additive	Conductivity (S/cm)
Sodium dodecylbenzene sulfonate 	9.9 (Omastova et al. 2003; Steiskal et al. 2003) 2 (Song et al. 2004; Shen and Wan 1998; Lee et al. 1995)
Dodecylbenzene sulfonic acid 	26 (Kudoh 1996) 8.30 (Omastova et al. 2003; Stejskal et al. 2003)
Sodium dodecyl sulfonate 	5.50 (Omastova et al. 2003; Stejskal et al. 2003)
Toluene sulfonic acid 	104 (Song et al. 2004)
Bis-2-ethylhexyl sulfosuccinic acid 	15 (Omastova et al. 2004) 7.3 (Stejskal et al. 2003) 27 (Boukerma et al. 2005)
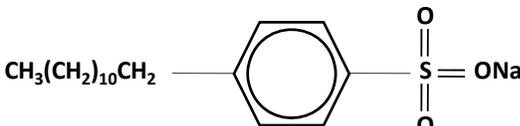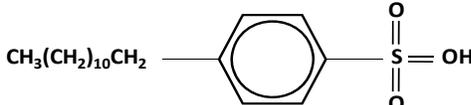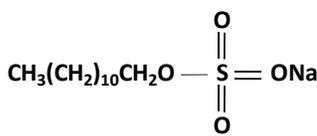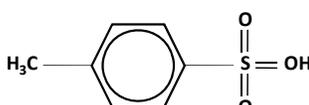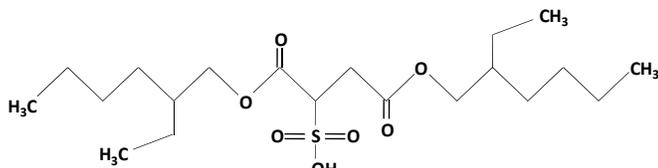
PPy particle size, shape and compactness can be modified by changing the additive type (Shen and Wan 1998) and the surfactant concentration (Prissanaroon et al. 2000). In most of the cases, globular, cauliflower-like PPy is obtained (Omastova et al. 1998; Lu and Pich 2004), thus showing that anionic additives (surfactants) mainly act as conductivity enhancer with a limited action on the PPy nanostructure. On the other hand, despite a null doping action, cationic surfactants (i.e. dodecyl- and cetyltrimethyl-trimethylammonium bromide) above the critical micellar concentration can form lamellar mesophases with the anions of the oxidising agent that act as templates for the formation of PPy nanofibers, as shown in Fig. 4 (Zhang et al. 2006).

PPy processability improvers

Among all the advantages of using additives, the increase of PPy processability has been one of the most attractive features. In fact, the PPy obtained after chemical synthesis is in the form of a black solid, insoluble in most of the solvents and unsuitable for moulding. Poor processability is, in fact, the key factor limiting the large-scale use of PPy.
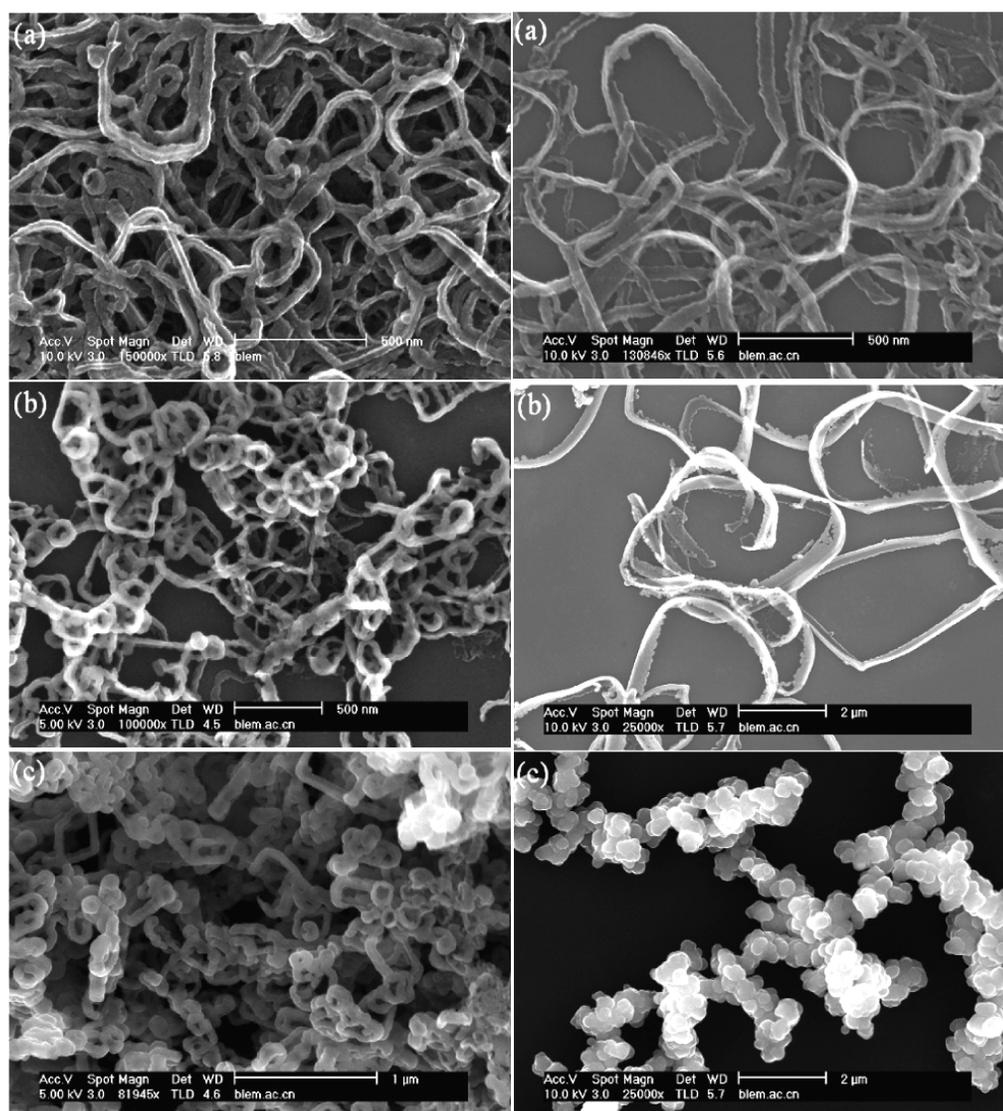
Fig. 4. PPy morphologies obtained by varying cetyltrimethylammonium bromide concentrations (left side pictures) (a)>(b)>(c), and by using different chain length surfactant salts (right side pictures): cetyltrymethylammonium bromide (a), dodecyltrymethylammonium bromide (b), octyltrymethylammonium bromide (c). Reprinted with permission from (Zhang et al. 2006). Copyright 2006, John Wiley and Sons.

Additives can help to overcome this problem in two principal ways: the first deals with the increase of PPy solubility, whereas the second concerns the production of PPy nanoparticles dispersible in many solvents or blends. The PPy insolubility originates from the strong intra- and inter- chains interactions, which impede polymer solvatation. When large molecule additives are used, they insert within the conducting polymer chains, thus reducing their interactions, and opening the PPy backbone (Lee et al. 1995). To render PPy soluble in different solvents, various additives can been used.

Surfactants, such as alkyl benzene sulfonic acids, make PPy soluble in most of the organic weakly polar sovents (m-cresol, chloroform, n-methyl-2-pyrrolidone (NMP),

dimethyl sulfoxide (DMSO) (Shen and Wan 1998a; Shen and Wan 1998b; Song et al. 2000; Lee et al. 1997).

More polar additives (such as di(2-ethylhexyl) sulfosuccinic acid) are necessary to improve PPy solubility in alcohols (Oh et al. 2001). Shen and Wan demonstrated that additives with an important steric hindrance or with a long alkyl chain are more successful in solvating PPy when compared with smaller homologues (Shen and Wan 1998a) (Table 2). In all the cases, the PPy solubility depends on Py/oxidant and Py/additive ratios.

PPy nanoparticles (30 to 300 nm) dispersible in many solvents can be obtained by polymerising Py with a suitable polymeric stabiliser.

Table 2. Different Alkyl Benzene Sulfonic Acids Used for Py Polymerization **

Sulfonic acid	Structure	Solubility [a] in *m*-cresol	σ_{RT} (S/cm)	Charge carrier
p-Methylbenzene sulfonic acid (MBSA)	H₃C—⟨⟩—SO₃H	×	16.0	polaron and bipolaron
p-Hydroxybenzene sulfonic acid (HBSA)	OH—⟨⟩—SO₃H	O	11.0	polaron and bipolaron
p-Dodecylbenzene sulfonic acid (DBSA)	CH₃(CH₂)₁₁—⟨⟩—SO₃H	⊕	2.0	polaron and bipolaron
β-Naphthalene sulfonic acid (NSA)		⊕	18.0	polaron and bipolaron
5-n-Butylnaphthalene sulfonic acid (BNSA)		⊕	0.5	polaron and bipolaron
5-Sulfo-isophthalic acid (SIA)		O	3.0	polaron and bipolaron
8-Hydroxy-7-iodo-5-quinoline sulfonic acid (QSA)		O	3.0	bipolaron
Alizarin red acid (ARA)		O	8	bipolaron
Camphor sulfonic acid (CSA)		×	18	polaron and bipolaron
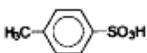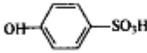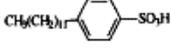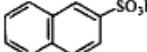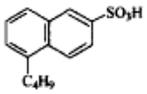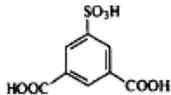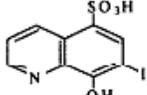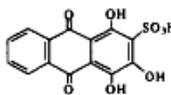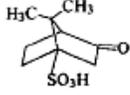
[a] ×, insoluble; ⊕, soluble; O, slightly soluble.

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These stabilisers can be commercially available, i.e. polystyrene sulfonate (Qi and Pickup 1997), polyvinyl alcohol (Armes et al. 1987; Men'shikova et al. 2003), or "tailor made", i.e. poly(2-vinyl pyridine-co-butyl methacrylate) (Armes et al. 1990). The stabiliser can be both adsorbed or segregated, during Py polymerisation, on PPy particles surface, and these core-shell particles are prevented from agglomerating by the additive's steric hindrance (Simmons et al. 1995). In this way, PPy colloidal dispersions can be redispersed in solvents in which the additive is soluble. Nevertheless, an excess of stabilizer can induce the encapsulation of PPy by a non conductive shell with a subsequent drop in charge transfer between PPy particles and conductivity (Sasso et al. 2008).

Defects in PPy

Even if the concentration of charge carriers in the doped PPy (as in most of the conducting polymers) is higher (two-fold to five-fold) than that of the inorganic semiconductors, the conductivity is approximately of the same order of magnitude. This depends, above all, on the higher defects concentration. These defects trap the electrons (in a potential hole), and, in many cases, the energy required to pass over the defect barrier is so high that carriers are stopped, and they cannot contribute any more to conductivity.

In PPy, defects are formed prevalently during the polymerisation, and they deal with conformational and chemical aspects. Concerning the conformational defects, out-of-plane bonding leads to a reduced π-orbital overlap, thus creating an obstacle to the regular sequence of single and double bonds. Chemical defects mainly include 2-3' and 2-4' couplings, and the formation of carbonyl and hydroxyl groups due to overoxidation (Skotheim and Reynolds 2007). Possible defects in the PPy chain are illustrated in Fig. 2.

PPY FILMS

Electrochemically Prepared PPy Films

Electrochemical PPy synthesis allows a direct film formation. It is indeed the most wide-spread and highly performing technique in term of conductivity. In fact, with this method it is possible to produce smooth, regular PPy films with outstanding conductivities (10^2 to 10^3 S/cm).

PPy films can be obtained without adding plasticizers, but their limitations in mechanical properties and difficulties in handling impede their use. So, to produce self-standing films it is necessary to overcome the PPy stiffness. For this purpose, two main methods have been reported. The first deals with the additives implementation during the polymerisation, thus obtaining homogeneous PPy-based composites. The second concerns the direct monomer polymerisation on a non-conducting substrate, thus producing composites with conducting-insulating interpenetrated networks.

The Py electropolymerisation with additives is indeed the most widely studied method because PPy-based composites with good conductivities (10 to 10^2 S/cm) and improved mechanical properties can be obtained (Skotheim and Reynolds 2007). Only the elongation at break remains inadequate. For instance, by electropolymerising Py with

different alkylbenzene sulfonic acids, films with Young's Modulus ranging from 0.1 to 1 GPa, a maximum elongation at break of 4% and a maximum conductivity of 90 S/cm, were produced (Bay et al. 2002).

PPy/non-conducting polymer composites can also be produced by monomer polymerisation on a non conducting substrate, i.e. polyvinyl chloride (Paoli et al. 1985); polyvinyldenefluoride-trifluoroethylene copolymer (Niwa et al. 1987); polytetramethyl-bis-phenol A carbonate (Kalaycioglu et al. 1996); polystyrene (Wang et al. 1990); or polyimide (Tieke and Gabriel 1990). This leads to the formation of layered structures with heterogeneous PPy concentration along the composite (Fig. 5). The process is based on the Py diffusion into the polymer film through the channel formed by the matrix swelling. The polymerisation starts at the interface between the polymer and the electrode, then it grows within the film, forming a so-called conducting alloy (Niwa et al. 1987).

Depending on the matrix, chemical interactions between PPy and the binder are formed during polymerisation. As a result, composites having properties that are different from the simple blend of the two polymers are produced (Kalaycioglu et al. 1996). With this technique, free-standing films having conductivity varying from 5 to 50 S/cm can be obtained (Kalaycioglu et al. 1996; Tieke and Gabriel 1990; Selampinar et al. 1994).

Despite the high conductivities reached by the films, the low quantities obtained in a given operation limit electropolymerisation use to the laboratory scale. Moreover, in the case of the alloy composites, the difficulty in controlling the PPy growth, mixing with the matrix, and the heterogeneity of the products obtained impede their large-scale production.
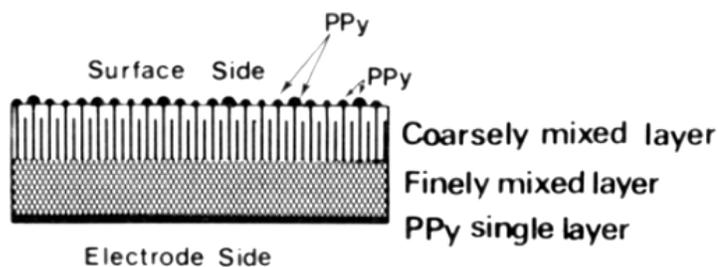

Fig. 5. PPy/non conducting film alloy: PPy growth occurs from the electrode to the film surface in a non homogeneous way. Reprinted with permission from (Niwa et al. 1987). Copyright 1987, American Chemical Society

Chemically Prepared PPy Films

To overcome the large-scale production problems encountered with the electrochemical PPy films production, several methods have been tested in the last decades. They were all based on the use of chemically synthesised PPy.

PPy appropriately modified (polymerisation with additives or chemical substitution) can be solubilised or dispersed in different solvents, and films can be obtained by casting technique or by spin coating in high quantities.

Depending on the solvent used, films obtained by spin coating PPy solutions on glass exhibit conductivities ranging from 10^{-2} to 2 S/cm after solvent removal. In fact, the solvent modifies the interactions strength between the polymer and the counterions during the drying process, thus affecting the PPy chains stacking and the charge hopping

between them. Song et al. (2000) demonstrated that, starting from the same PPy particles (1 S/cm), films obtained from dimethylsulfoxide and chloroform showed a difference in conductivity of two orders of magnitude, being the conductivity values 1.6×10^{-2} S/cm and 1.7 S/cm for the two solvents, respectively. Similarly, not volatile additives can act as secondary dopants, remaining included in the PPy chains and modifying PPy stacking and conductivity (Lee et al. 2000).

In general, films obtained from soluble PPy are less rigid than those prepared electrochemically. They present a lower modulus, but improved elongation at break (Lee et al. 2000). Indeed, the enhanced flexibility of the PPy chain, produced by the additive insertion, favours the production of more flexible films. Compared to their homologues obtained electrochemically, they present a smoother surface (Song et al. 2000).

Despite the possibility of a large-scale production, this technique presents some drawbacks, mainly due to the low conductivity achieved and the extensive use of polluting organic solvents. Indeed, leaving aside the film forming stage, the synthesis of unsubstituted pyrroles can be carried out in water by the condensation of 1,4 dicarbonyl compounds with primary amines, also known as the Paal-Knorr method (Amarnath et al. 1991; Gilchrist 1998) or in vapour phase, where ammonia and furan (a furfural derivative) vapors come into contact with an acidic catalyst, i.e. Al_2O_3 (Elming and Clauson-Kaas, 1952, Harreus, 2002). On the other hand, substituted pyrroles, which are used as precursors for the polymerisation of soluble PPy, are synthesised in organic media (Amarnath et al. 1991).

To limit the use of organic solvents, other techniques, involving the production of PPy/non-conducting polymer composites, have been proposed. In this way, besides the process environmental improvement, composites having specific properties, particularly in mechanical terms, can be obtained (Cassignol et al. 1999).

PPy direct synthesis on a preformed polymeric matrix allows the production of composites having improved mechanical properties through a low-polluting process. These composites can be achieved by dipping the conventional polymer film (containing the oxidant) onto the monomer solution (impregnation method) (Mandai and Mandai 1996; Wang and Fernandez 1992; Chakraborty et al.1999; Migahed et al. 2004; Yang et al. 1996; Bhattacharyya et al. 2000), or by exposing it to monomer vapours (vapour-phase method) (Bleha et al. 1999; Radhakrishnan et al. 1995). The use of volatile solvents such as tetrahydrofuran (THF) (Radhakrishnan et al. 1995; Chakraborty et al. 1999) or acetone (Wang and Fernandez 1992) is usually limited to the casting of the polymeric film.

Interpenetrated polymer network (IPN) composites, in which the PPy network is intimately interconnected with the matrix, are thus formed. Typical binder used are: poly(vinyl acetate) (Chakraborty et al. 1999); poly(vinyl alcohol) (Benseddik et al. 1995); poly(methyl methacrilate) (Mandai and Mandai 1996); poly(imide) (Tieke and Gabriel 1990); poly(vinyl methyl ketone) (Chakraborty et al. 1999); and poly(ethylene) (Radhakrishnan et al. 1995). As in the case of PPy/polymer alloys obtained electrochemically, PPy diffuses within the channel formed by the swelling, and it grows within the matrix, forming a capillary three-dimensional network. But, in contrast to the above mentioned alloys, in this case more homogeneous films are obtained.

For these composites it was reported that the percolation threshold ranges between 2 and 10% (Mandai and Mandai 1996), which is much lower than the value predicted for conventional blends, namely 16% (Zallen 1983). The dendritic distribution of the conducting polymer is, in fact, much more anisotropic in this case if compared with that in a random blend.

The conductivity for this kind of composites is normally between 10^{-4} and 1 S/cm, which is significantly lower than those obtained for their electrochemically synthesised homologues. Only Yang et al. (1996) obtained PPy/polypropylene (PP) composite films with conductivity up to 6.7 S/cm. A microporous PP membrane was laminated between two solutions: one containing Py and dodecyl benzene sulfonic acid, while the other was based on $FeCl_3$. Conductivities varying from 0 to 6.7 S/cm were obtained by modifying the polymerisation parameters (such as $FeCl_3$ and Py concentration, and polymerisation time). Such films presented remarkable mechanical properties: Young's modulus of 0.4 to 0.8 GPa, and elongation at break of 90 to 200%.

Another technique that greatly reduces the requirement to use polluting solvents and at the same time makes it possible to produce freestanding well-conducting PPy composite films is the compression moulding of PPy/insulating polymer core/shell particles (Fig. 6) (Omastova et al. 1996, 1998, 1999; Jang and Oh 2005). PPy is synthesised in a water (Yang et al. 1996) or water/methanol (Omastova et al. 1999) solution containing the insulating polymer (or a surfactant), and the collected particles are then pressed at high temperature to obtain handling composites with conductivity up to 10 S/cm. The composite electrical properties can be increased by doping PPy with iodine during its synthesis, thus obtaining conductivities up to 116 S/cm (Jang and Oh 2005).
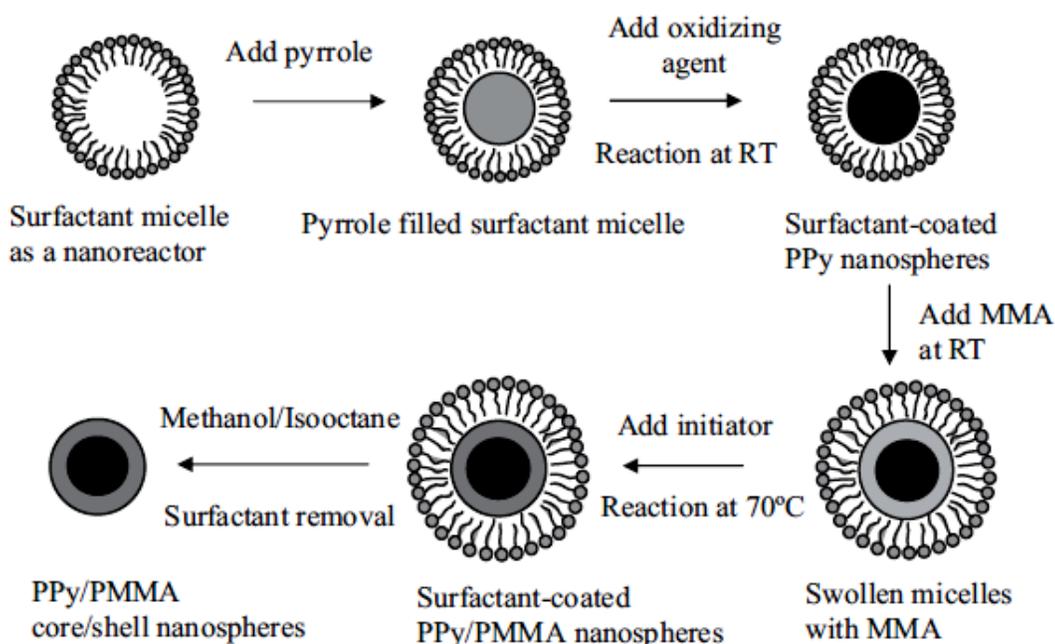

Fig. 6. Diagram of the preparation process of PPy/PMMA particles. Reprinted with permission from (Jang and Oh 2005). Copyright 2005, John Wiley and Sons.
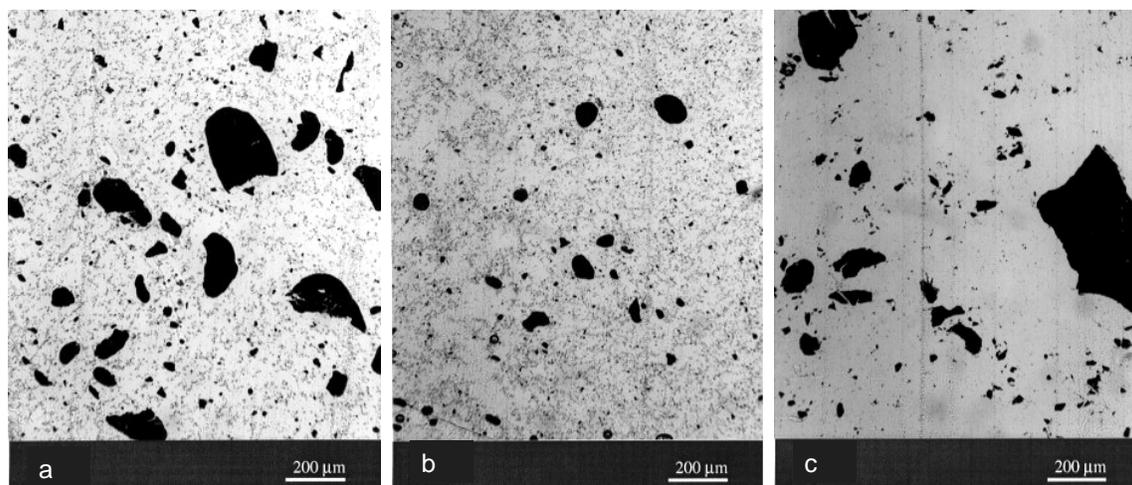
Fig. 7. PPy particles in epoxy resin after dispersion with (a) turax; (b) ultrasound; (c) wing mixer. Reprinted with permission from (Cassignol et al. 1999). Copyright 1999, Elsevier

Finally, a method presenting several advantages in the large-scale PPy production over the above mentioned techniques is mixing. Preformed PPy particles are mixed to a melt/dissolved non-conducting polymer matrix (Hacarlioglu et al. 2003; Cassignol et al. 1999; Bhat et al. 1999; Balci et al. 1995), and after solvent drying, PPy/insulating polymer blends are obtained.

With this method, homogeneous conducting PPy-based films with no limitation in thickness and mechanical properties can be produced, depending on the matrix chosen. Concerning the conductivity, it was demonstrated that the particle size, particularly the particle tendency to agglomerate, greatly influences the percolation and consequently the conductivity of the final film (Cassignol et al. 1999). In fact, PPy particles produced with a steric stabiliser have a higher tendency to form clusters than particles obtained without additive. Once in the blend, the additive-issued PPy particles would agglomerate, thus increasing the percolation threshold in comparison with the additive-free particles. As a consequence, the dispersion method of the conducting particles in the matrix becomes essential to yield composite films with high conductivity. Vigorous stirring (with ultrasound or turax) showed the best results (Fig. 7). Although the mixing technique leads to films with a lower conductivity (up to 10^{-1} S/cm) compared to the electrochemically synthesised composites, it presents several advantages. From an industrial point of view, the described approach allows a massive production of PPy conducting films, employing more environmentally friendly conditions than the other techniques. Moreover, the process is simple and easy to implement (Table 3). A scheme of Py polymerisation procedures to produce the over mentioned film is shown in Fig. 8.

PPy Applications

Owing to its typical poor solubility, today PPy can find a marginal application in anticorrosion coatings (Tallman et al. 2002). Nevertheless, recent works showed that new synthesis routes can open to PPy a broad range of potential applications in different fields thanks to its electrochemical and conducting properties.

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Table 3. Electrical and Mechanical Properties of PPy-based Films Obtained by Electrochemical and Chemical Synthesis with Relative Possibility of High-volume Production

Synthesis	Type	Conductivity (max) S/cm	Mechanical properties	High-volume production
Electrochemical	PPy films	+++ (10^3)	- - -	- -
	Py electropolymerisation on preformed plastic film	++ (50)	+	- -
Chemical	Soluble/dispersible PPy	+ (5)	++	-
	PPy/insulating polymer composites by compression moulding	++ (10)	++	++
	PPy/insulating polymer composites by mixing	+ (1)	++	+++
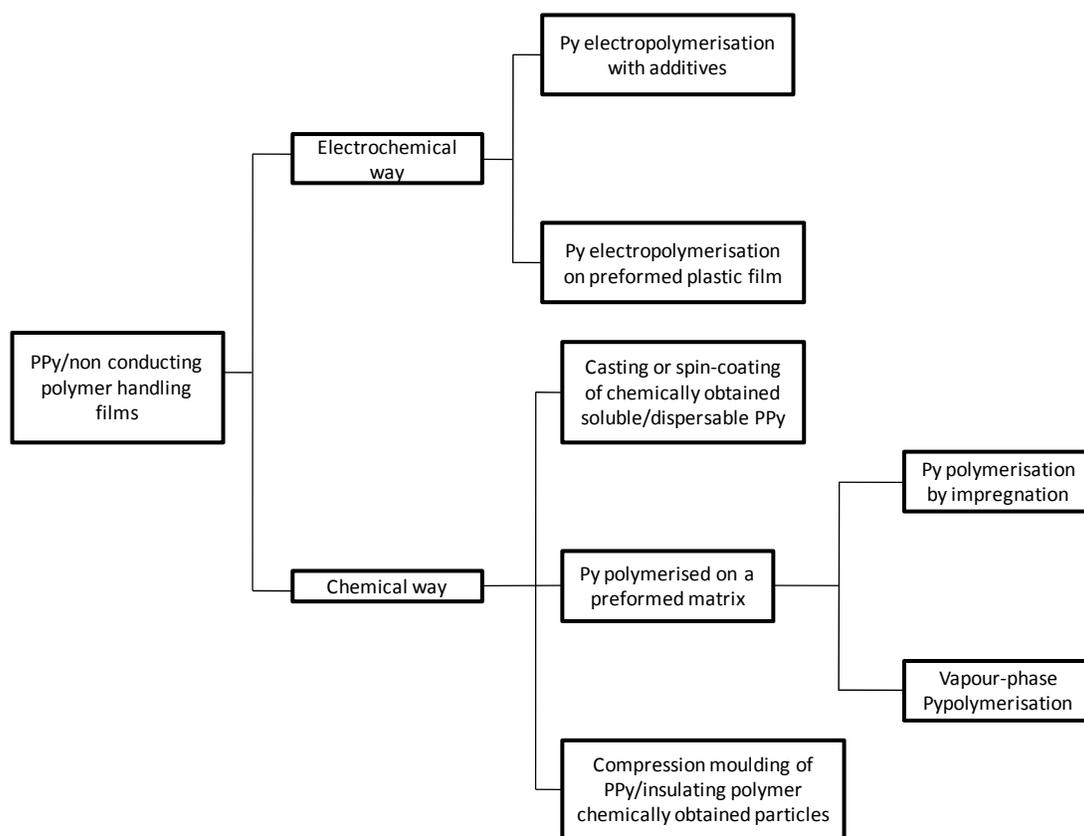
Fig. 8. Summary of possible techniques for preparing PPy films

 PPy or PPy-based composites have been proposed as electrode materials for energy storage devices (electrochemical batteries and capacitors), electrocatalysts and biosensors, photo-luminescent materials, artificial muscles, gas separating membranes, anticorrosive coatings, electromagnetic shields, materials for organic electronic devices (transistor electrode or active channel), and so forth. In this section, the working principles (and the PPy function) of the most promising applications are presented.

Sensors

A sensor is a device that transforms the concentrations of analytes to other detectable physical signals (currents, absorbance, mass, or acoustic variables). In the case of PPy, the interactions between the analyte and the polymer correspond to oxido-reduction reactions. These redox reactions are associated with a change in PPy doping level and consequently to a change in PPy conductivity (Bai and Shi 2007). This conductivity variation is detected and transformed into analytical results. A possible technology for a gas sensor is proposed in Fig. 9.

It was reported that PPy can be used as a sensor for certain components in gas, such as inorganic (NO, CO_2, CO, NH_3, H_2S) (Hernandez et al. 2007; Liao et al. 2005; Waghuley et al. 2008) and organic molecules (acetone, methanol, ethanol) (Melo et al. 2005). pH or vapour sensors can also be produced. Moreover, immobilization of active molecules on PPy, such as glucose oxidase (Sung et al. 2004; Ekanayake et al. 2007), has been used to develop bioanalytical sensors for glucose, DNA, and proteins sensing (Ramanavicius et al. 2006).

Actuators

An actuator is a device capable of converting electrical energy into mechanical work. PPy is suitable to produce actuators because it can show a dimensional change. In fact, depending on its oxidation state, counter-ions are attracted or expelled from the PPy film in order to maintain charge neutrality, thus inducing a volume variation (Skotheim 2007; Madden et al. 2000). So, when an electric field is applied, the cations and the anions would move through the anode and the cathode, respectively, thus producing a mechanical deformation of the film. The most developed field of application of PPy-based actuators is in biomedical components for the production of artificial muscles (Otero and Cortes 2003).
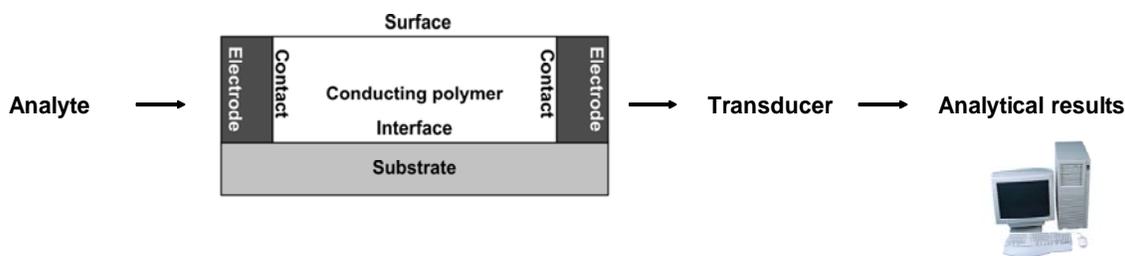

Fig. 9. Possible technology for a PPy-based gas sensor

Batteries

A rechargeable battery is a device that can convert chemical energy into electrical energy and vice-versa. It is composed by two electrodes, positive and negative, and an electrolyte. The two electrodes ensure the electron movement, while the electrolyte acts as a buffer for the ion flows between the two electrodes. Due to its capacity for charge storage (Song and Palmore 2006; Killian et al. 1996), in a rechargeable battery, PPy has been proposed either as a positive (Wang et al. 2005) or a negative (Guo et al. 2005) electrode (Fig. 10). It has been studied also as an electrode and electrolyte for capacitors (Kim et al. 2006b).

Organic thin film transistors (OTFT)

A transistor is a three-terminal device capable of switching or amplifying an electrical current. A field-effect transistor (FET), the most common type of transistor, is composed by three parts: an insulator, a thin semiconducting layer (the active channel), and three electrodes. The source and the drain electrodes (made of n-doped Si in n-type FET) act as conventional electrodes, ensuring the flow of charge carriers to the device. The gate electrode (made of p-doped Si in n-type FET), as a function of its potential with respect to the source, can form a conducting or an insulating channel between the source and the drain electrode (Klauk 2006). The flow of electrons (or electron holes) from the source to drain is controlled by the voltage applied across the gate. In this kind of device, PPy can be used as electrode, but also as an active channel, depending on the targeted conductivity (Bjorklund and Liedberg 1986; Kou and Liou 1996).
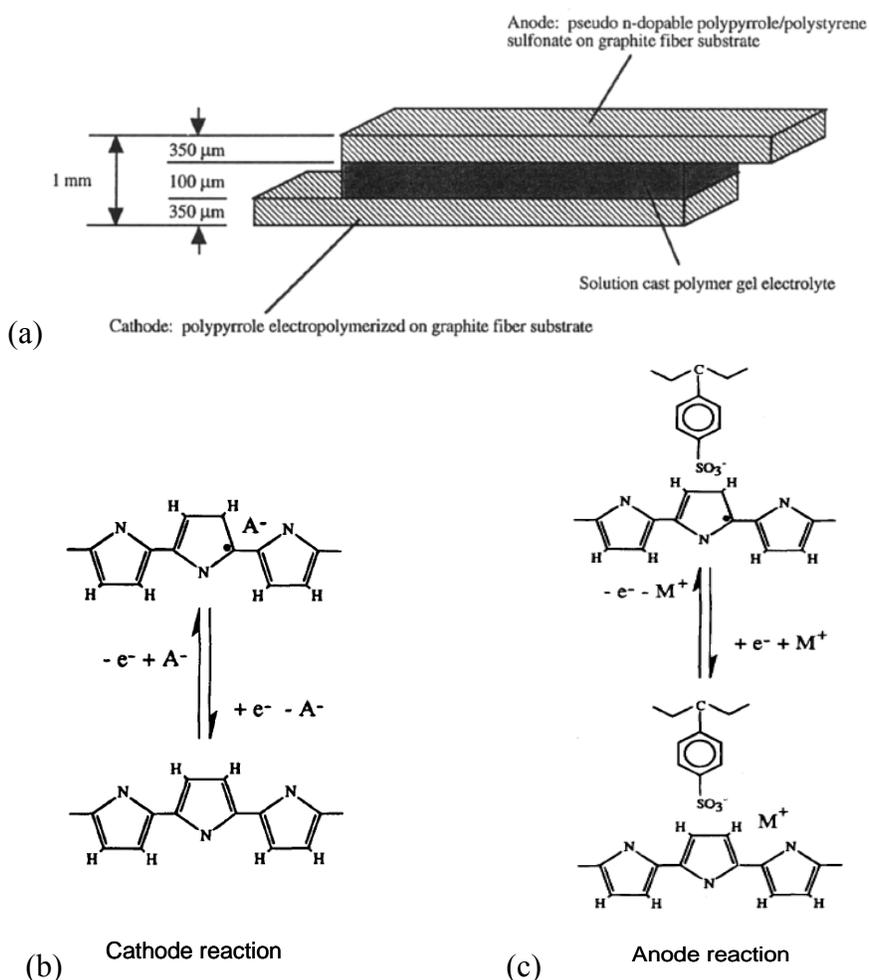
Fig. 10. Possible configuration of a PPy based battery (a), and cathode (b), and anode (c) reactions. Reprinted with permission from (Killian et al. 1996). Copyright 1996, The Electrochemical Society

PPY COMPOSITES WITH FIBROUS WOOD-DERIVED MATERIALS

Py Polymerisation on Fibres and Wood Particles

The polymerisation of Py on cellulose fibres surface leads to processable conducting fibres that can be used to form conducting paper (Huang et al. 2006a,b) or to reinforce a thermoplastic matrix (Micusik et al. 2006).

PPy-coated fibres can be obtained by two methods: i) Py dispersion polymerisation (cellulose fibres, monomer, and additives are dispersed into water, then the oxidant solution is added) (Johnston et al. 2006; Micusik et al. 2006; Kelly et al. 2007; Ding et al. 2010a; Beneventi et al. 2006), and ii) by Py vapour-phase polymerisation on fibres (Hosseini and Pairovi 2005; Esfandiari 2008). In both cases, PPy particles form a layer of about 100 to 200 nm thick on the fibres surface (Johnston et al. 2006; Hosseini and Pairovi 2005). Py would be linked to the fibres thanks to hydrogen bonds between the amine groups of Py and the hydroxyl surface groups of cellulose (Johnston et al. 2005).

These composites, in the form of compressed paper sheets, have conductivities ranging between 10^{-8} and 1 S/cm, depending on the polymerisation conditions.

The PPy coating morphology and, consequently, conductivity, are affected mainly by reactant initial concentrations (Ding et al. 2010a; Beneventi et al. 2006; Kelly et al. 2007; Micusik et al. 2006; Huang et al. 2005). Ding reported that by increasing the monomer content in the initial mixture, the covered area of the fibres surface increases, inducing a conductivity enhancement (Fig. 11). The same behaviour was reported for the oxidant (Beneventi et al. 2006). The fibre surface and bulk properties were shown to affect the composites conductivity too. In fact, by comparing PPy/cellulose composites obtained with lyocell and viscose fibres, different fibre reactivity with respect to PPy and final conductivity were observed (Dall'Acqua et al. 2004). Indeed, the presence of a smooth surface and the higher Py penetration in amorphous zones favoured the formation of a continuous conducting PPy-phase in viscose fibres with respect to Lyocell fibres bearing larger crystallites than viscose and a crackled-fibrillated surface.

In order to improve composite conductivity, fibres have been charged with metal particles or with other additives. Interestingly, it was demonstrated that with the addition of silver particles, the conductivity of PPy/cellulose fibres was not improved (Kelly et al. 2007). On the contrary, it seems that when additives such as dodecyl benzene sulfonate (Johnston et al. 2006) or toluenesulfonic acid (Ding et al. 2010b) were used during Py polymerisation, the PPy covered the fibres more uniformly (Johnston et al. 2006) compared with the additive-free PPy. The consequence is an improved conductivity. Homogenoeus, nanometric PPy layers (20 to 25 nm) have been obtained through Py polymerisation on the fibres surface by impregnating them with the supernatant of a reactive oxidative Py polymerisation bath (still containing reactive species and oxidant) (Huang et al. 2005).

The conducting fibres thus obtained (at increasing PPy amount) have been used by Mičušík to reinforce polyolefin (linear low-density polyethylene, LLDPE, and high-density polyethylene, HDPE) or polycaprolactone (PCL) matrices in order to obtain conducting composites for antistatic applications (Micusik et al. 2006).
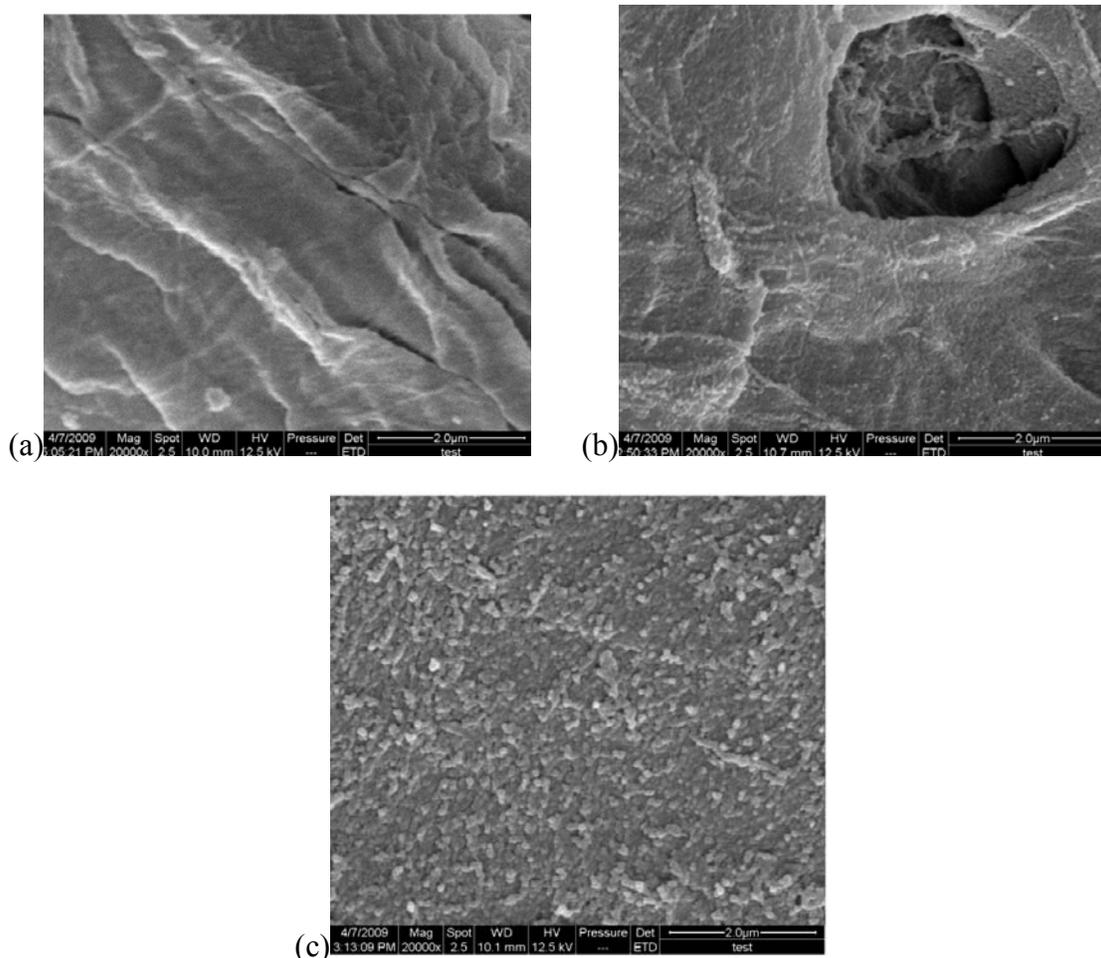
Fig. 11. Pulp fibres coating by PPy at different monomer concentrations. Untreated cellulose fibres (a) and PPy-coated fibres prepared in presence of 1.5 g/L (b) and 5 g/L of pyrrole (c) with a constant monomer to oxidant (FeCl$_3$) ratio of 1:2. Reprinted from (Ding et al. 2010a)

It was reported that the conducting and mechanical properties depend essentially on the matrix (Fig. 12). The best conductivities obtained (with PCL matrix: 6.5x10^{-4} S/cm) fall in a range suitable for electrostatic charge protection applications.

Wood particles, such as sawdusts, have also been used to prepare PPy/fibres conducting composites. Cheap adsorbent materials for polluting solvents (Ansari and Fahim 2007; Ansari and Delavar 2008) or shielding components for electromagnetic radiations (Sapurina et al. 2005) were then produced. These composites were obtained by dispersion polymerisation of Py in a system containing the wood sawdust (previously impregnated with the monomer) and the oxidant.

Thanks to the PPy ion exchange properties, PPy/sawdust composites succeed in trapping anionic contaminants, such as Cr(VI) (Ansari and Fahim 2007) and As (Ansari and Delavar 2008): the ion dopant deriving from polymerisation (Cl$^-$, for instance) is replaced by the polluting metal anion. PPy/wood sawdust composites can be applied in water or effluent treatment technology.
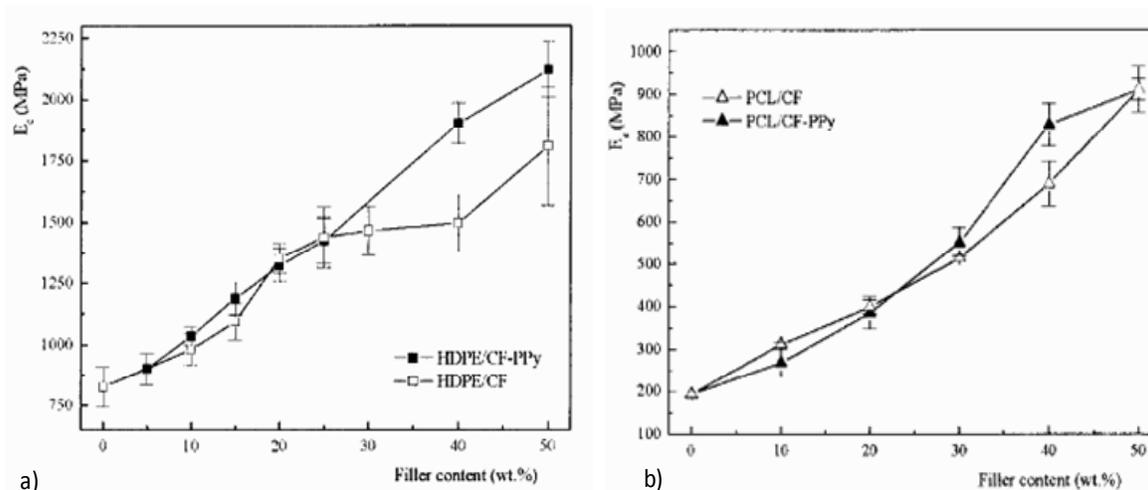
Fig. 12. Composites Young's modulus (*Ec*) of a) HDPE filled with untreated cellulose fibres and PPy/cellulose fibres (20.6% PPy); b) PCL filled with untreated cellulose fibres and PPy/cellulose fibres (20.6% PPy). Reprinted with permission from (Micusik et al. 2006). Copyright 2006, John Wiley and Sons

As PPy exhibits good properties in absorbing electromagnetic waves (it can both absorb and reflect the radiation, while metals only reflect these waves). PPy/sawdust composites were proposed as construction materials for screening the electromagnetic radiation (Sapurina et al. 2005). It was demonstrated that thick layers of about 100 mm were required for this purpose.

Py Polymerisation on Paper Sheets

Paper-like/PPy composites have attracted great attention because of the possibility of associating the electrochemical properties of PPy with the mechanical/physical properties of paper. Flexible and lightweight, conducting composites with outstanding oxido-reduction properties can, in fact, be produced.

Normally, they are obtained by the sequential impregnation of paper (filter paper, handsheets, etc.) into the monomer and the oxidant solutions (or *vice-versa*). As in the case of the previously described composites, the electrical and morphological properties depend on the polymerisation conditions (Johnston et al. 2005; Bjorklund and Lundstrom 1984; Huang et al. 2005, 2006b). The conducting polymer encapsulates the wood fibres with a layer of 50 to 150 nm thickness, and composites with conductivity ranging from 10^{-10} to 6 S/cm are obtained. These conductivities are supposed to derive from the fibrous composition of paper. Fibres would provide a pathway for the growth of PPy chains, thus allowing them to orient themselves along the principal axis of the fibrous material in a quite regular way. Good conductivities were thus obtained (Bjorklund and Lundstrom 1984). Compared to other conducting polymers, it was reported that PPy has a better affinity to paper than poly(aniline) (Johnston et al. 2005; Richardson et al. 2006). PPy/paper composites, in fact reaching conductivities up to 6 S/cm, while poly(aniline)-homologues show much lower values, i.e. 10^{-3} S/cm (Johnston et al. 2005).

As an alternative to liquid phase deposition of PPy on paper sheets, vapour phase deposition (Quian et al. 2010) and ink jet patterning (Winther-Jensen et al. 2007), based

on the sequential impregnation of paper with the oxidant, its exposure to Py vapour, and the subsequent Py polymerization, have been successfully used to produce both conductive papers with good electromagnetic shielding effectiveness (ca. 25 dB between 0.5 and 1.5 GHz) and accurate PPy conductive patterns on copy paper, respectively.

The possibility of combining the high specific surface area of cellulosic fibres with the electrochemical properties of PPy makes PPy/cellulose fibres composites really interesting for applications based on ion exchange ability, such as charge storage devices and sensors.

Several studies have been recently proposed with the aim of characterising and improving the ion exchange ability of PPy/cellulose fibres composites for battery applications. In particular, different cellulose derivatives with micro- and nano-fibrillar structure, such as Cladophora (Mihranyan et al. 2008; Gelin et al. 2009; Stromme et al. 2009; Razaq et al. 2009; Nystrom et al. 2009) or microfibrillated (MFC) (Nystrom et al. 2010; Sasso et al. 2010a) celluloses, were investigated. To date, the system with Cladophora cellulose has been more deeply investigated. It was demonstrated that, depending on the oxidant, the morphology and the anion exchange properties of the composite were greatly affected. $FeCl_3$ was compared with phosphomolybdic acid (Razaq et al. 2009). The former, being a milder oxidant than the latter, preserved the microfibrillar structure of the cellulose, thus resulting in an almost a two-fold increase in specific area (59 m²/g vs. 31 m²/g) (Fig. 13).

Conductivity was also affected: a value of 0.65 S/cm was obtained for $FeCl_3$ composites and 0.12 S/cm for the phosphomolybdic acid homologues. The electrochemical properties of the Cladophora- and MFC-based composites in the presence of electrolyte solutions containing different ions were further studied (Gelin et al. 2009; Stromme et al. 2009), and batteries with promising charge storage capacity were prepared (Nystrom et al. 2009). The system PPy/MFC presented even higher specific area (89 m²/g), conductivity (1.5 S/cm) and good ion exchange ability (Nystrom et al. 2010).
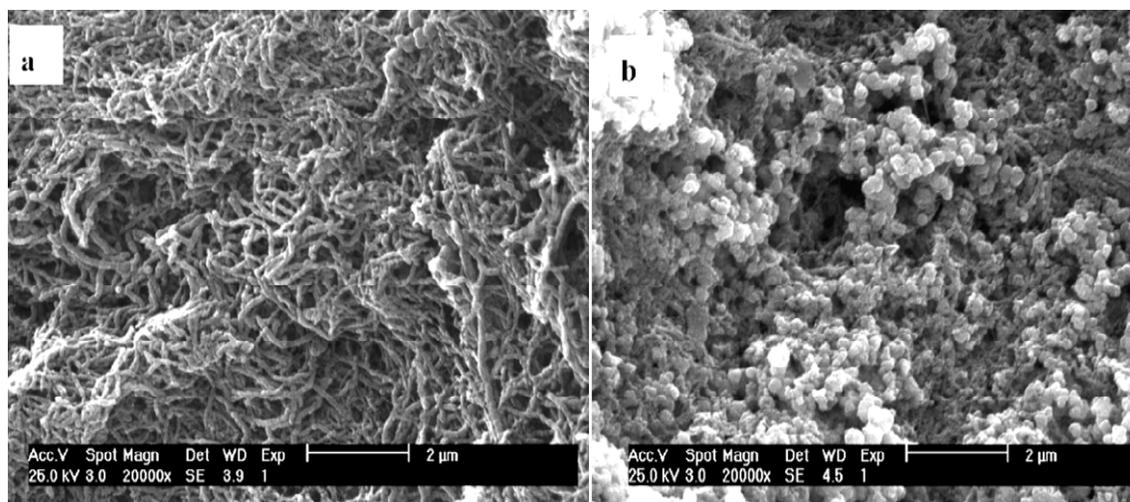

Fig. 13. Impact of the oxidant type on PPy/cellulose fibrillar structure: a) $FeCl_3$, b) phosphor-molybdic acid. Reprinted with permission from (Razaq et al. 2009). Copyright 2009, American Chemical Society
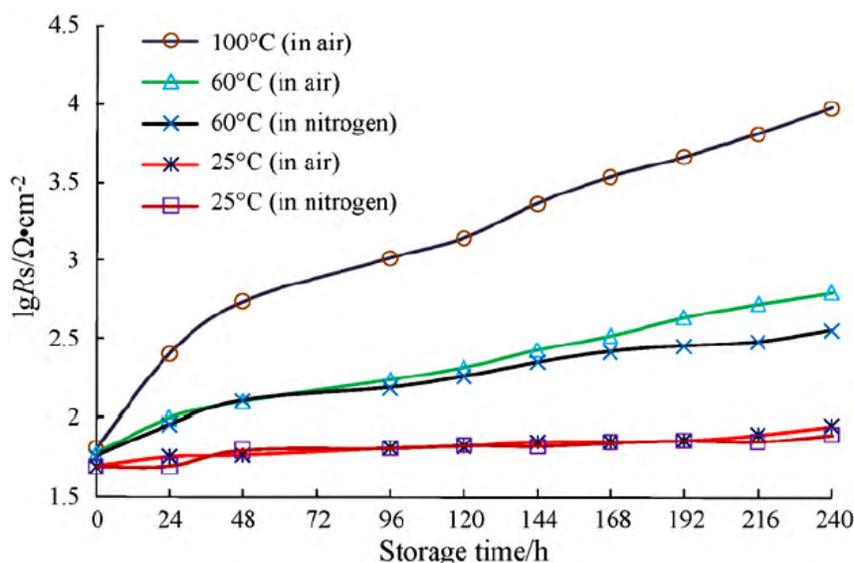
Fig. 14. Impact of temperature and atmosphere on PPy/paper composites resistivity (inverse of conductivity). Reprinted with permission from (Li et al. 2010). Copyright 2010, Elsevier

Other than batteries, the ion exchange properties of PPy/paper composites can be exploited for the production of cheap and accurate pH sensors (Yue et al. 1996). These devices were prepared by soaking common copy paper (70 g/m^2) in $FeCl_3$ and Py solutions. Precise pH measurements were recorded in the 5 to 10 pH range.

Indeed, one of the most important problems for composites applications is the PPy stability. It has been recently reported that electrochemical PPy properties are greatly affected by the temperature and the alkalinity (Li et al. 2010). In fact, conductivity decay is more pronounced in a basic environment, where the electron-donor species induce a decrease of the charge carriers, and at high temperature (for both air and nitrogen atmosphere), due to the over-oxidation of the conjugated system (Fig. 14). Moreover, owing to the hygroscopic character of cellulosic materials, PPy/cellulose composites display a high sensistivity to relative humidity (i.e. conductivity increases with relative humidity) and PPy/Cladophora cellulose composites have been proposed for moisture sensor applications (Mihranyan et al. 2008).

PPY COMPOSITES WITH SOLUBLE MACROMOLECULAR WOOD-DERIVED MATERIALS

Py Polymerisation with Wood Derivatives as Additives

Despite their varied chemical composition and large availability, the use of soluble macromolecular wood derivatives in the PPy synthesis has not been developed so far.

Alkyl cellulose ethers have been proposed as stabilisers and conductivity enhancers for Py polymerisation. Thus, in 1986, Bjorklund used methylcellulose (MC) as an additive for the aqueous oxidative polymerisation of Py in the presence of iron (III) chloride (Bjorklund and Liedberd 1986). A colloidal PPy/MC aqueous dispersion, in

which MC disposed around PPy in a core-shell structure, was obtained. These dispersions were then conditioned as films, and the conductivity of such composites (obtained by varying the oxidant, i.e. $FeCl_3 \cdot 6H_2O$, and additive concentrations) ranged from 10^{-9} to 0.2 S/cm. MC was also used by Yoon to prepare $PPy\text{-}SnO_2\text{-}MC$ nano-suspensions for electrorheological fluids (Yoon and Kim 2006). Particles with diameter between 80 and 200 nm, and with an average surface area of around 204 m²/g were obtained.

Furthermore, good results in producing colloidal PPy in water and water/alcohol medium using $FeCl_3$ as oxidant were obtained with hydroxypropyl cellulose (Amaike and Yamamoto 2006) or ethylhydroxy-ethylcellulose (EHEC) (Mandal and Mandal 1995), respectively. It was demonstrated that EHEC acted as a more efficient stabiliser in water/methanol mixture compared with a pure water medium. Particularly, a bimodal size distribution (originating from the aggregation or not of metastable particles) was observed by transmission electron microscopy: the first class was around 20 nm and the second one ranged from 40 to 160 nm (Mandal and Mandal 1995). The formation of small PPy particles depended on the oxidant used ($FeCl_3$ or APS). Systems having fast oxidation kinetics (e.g., APS) would induce PPy metastable particles to be adsorbed on more stable PPy agglomerates, while, for slow kinetics systems, the slower PPy nuclei formation allowed EHEC to absorb on their surface, thus stabilising them. Despite the gain in dispersability, PPy/EHEC pellets presented lower conductivity than their PPy (without EHEC) homologues (17 vs. 25 S/cm). In these systems, the best electrical properties were obtained for particles produced in water medium.

Recently, lignosulfonates (LS) and carboxymethylcellulose (CMC) have been found to be good dispersants for PPy particles in aqueous medium (Yang and Liu 2009; Sasso et al. 2008; Sasso et al. 2011). By increasing the LS and CMC concentration during Py polymerisation, the resulting PPy particles were smaller and better separated. The interaction between LS, CMC, and Py during polymerisation would affect also PPy particles conductivity and the polymerisation mechanism. It was shown that conductivity of PPy pellets increased with the LS amount, and then it remained constant for some concentrations before decreasing due to the excessive amount of non conducting material. XRD analysis showed that the structure of highly LS-containing PPy was more ordered than that fed with lower amount of LS. According to the author, this feature was associated with the alignment of PPy chains due to the LS molecules acting as a linear template for PPy growth. The difference in structural order between high and low LS-containing PPy corresponded to different charge transport mechanism.

Py Polymerisation in the Presence of Wood Derivatives for Conducting Films Production

Usually, PPy/cellulose derivatives films are obtained by Py vapour phase/ impregnation polymerisation on a preformed cellulose film, or electrochemically.

PPy/cellulose derivatives films obtained by vapour phase pyrrole polymerisation have been produced with carboxymethyl cellulose (Yin et al. 2001) and cellulose diacetate (Li et al. 2006) as matrices. The main problem linked to this kind of composites is the PPy heterogeneous growth within the film.

In fact, it was demonstrated that the bottom and air surfaces of the films presented different conductivity (Yin et al. 2001). To overcome this problem, cellulose films were

produced with solvents more swelling than water, such as chloroform, methanol, or tetrahydrofuran, thus creating a higher surface area for PPy to grow. In this way, the final PPy mass in the film was increased, thus inducing an enhanced composite conductivity (from 10^{-3} S/cm to 10^{-1} S/cm). Another proposition to improve the homogeneity of PPy distribution within the composite was to initiate Py polymerisation with supercritical carbon dioxide (Li et al. 2006). In fact, compared to the classical vapour phase synthesis, this technique led to an improved swelling of the cellulosic film, thus allowing a uniform PPy growth in the matrix pores. A conductivity gain of one order of magnitude was observed (10^{-1} S/cm).

Wood derivative conducting films obtained by Py impregnation polymerisation, in mass (Bhat et al. 1999) or on the film surface (Mahadeva and Kim 2010), showed promising properties for the production of sensors or electromechanical actuators (Mandaeva and Kim 2010; Kim et al. 2006a). Cellophane was the elected material for these applications.

Cellophane (without PPy), having remarkable piezoelectric properties, was used for the production of the electroactive paper (EAPap), a material that shows a bending displacement when subjected to an electric field. The use of PPy would increase the performance of this device, by supplying a further volume change due to the ions displacement during oxido-reduction reactions (Cho et al. 2008). Compared with the simple cellophane, PPy/cellophane composites presented a displacement more than twice better (from 4 mm to 9 mm). This behaviour was further improved when ionic liquids were added to the composites (10 mm of displacement) (Mandaeva and Kim 2010).

PPy/cellophane composites for EAPap applications were also obtained by Py electropolymerisation on the cellophane surface (Deshpande et al. 2005a,b). These composites showed quite similar properties of displacement (9 to 10 mm) compared with their chemically obtained homologues. PPy/carboxymethyl cellulose (CMC) composite films, with conductivities ranging from 10 to 40 S/cm and $7x10^{-2}$ S/cm were produced by polymerising pyrrole in presence of CMC by electrochemical polymerisation (Mahmud et al. 2005; Otero et al. 1998) and chemical polymerization followed by the addition of CMC as a film forming agent (Sasso et al. 2011), respectively.

Fairly recent investigations demonstrated that the addition of film-forming cellulose derivatives, i.e. CMC (Sasso et al. 2011), MFC (Sasso et al. 2010a), and carboxylated microcrystalline cellulose (Rußler et al. 2011) during PPy polymerization does not make it possible to obtain self-standing conductive films owing to CMC complexation (Sasso et al. 2010b) and both MFC and carboxylated microcrystallyne cellulose gels disruption in the reaction medium. The mixture of preformed PPy and film forming cellulose derivatives appears the most effective method for casting bulky conductive films. Moreover, the use of MFC instead of soluble CMC as film forming agents prevented the encapsulation of conducting particles by a non conductive (CMC) shell and, as shown in Fig. 15, promoted the formation of interpenetrated continuous networks composed by conductive PPy and film forming MFC, respectively (Sasso et al. 2010a).
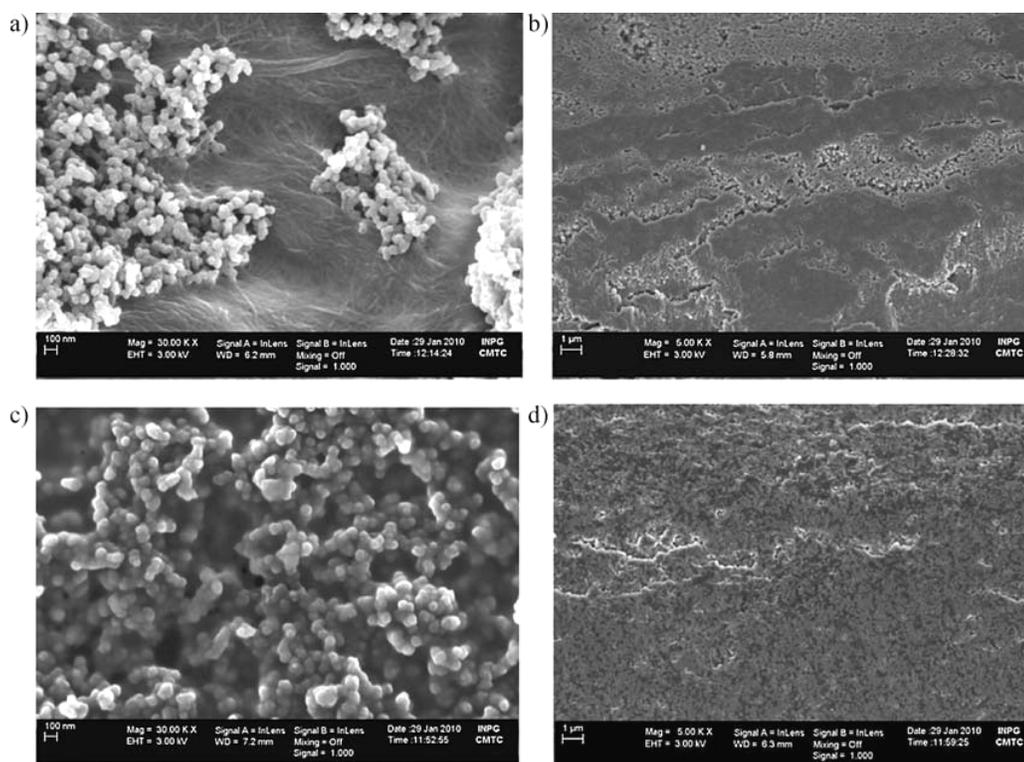
Fig. 15. SEM images of PPy/MFC (a,b) and PPy/CMC conducting films obtained by casting aqueous dispersions of PPy in the presence of a film forming agent, i.e. MFC of CMC. Reprinted from (Sasso et al. 2010). Copyright 2010, Wiley

CONCLUDING REMARKS

Intense research work carried out on the use of cellulose fibres and woody polymers for the elaboration of PPy-based conducting composites has demonstrated that this class of biosourced materials represents a viable alternative to synthetic polymers derived from fossil resources.

In particular, papermaking/textile fibres, nanofibrils, and water-soluble cellulose/lignin derivatives can effectively substitute for most of the synthetic polymers that are currently used for both: i) the chemical synthesis of PPy aqueous dispersions and ii) the manufacturing of flexible conducting films/yarns.

Moreover, the use of cellulose fibres/nanofibrils either as substrate for PPy polymerization or unmodified binder, makes it possible to obtain new porous and flexible composite films bearing mechanical and electron transport properties close to those of paper and the pristine conducting polymer, respectively. In order to provide a snapshot of current approaches used for the elaboration of conductive polypyrrole/wood derived materials composites, Table 4 and Fig. 16 summarize the raw materials and conductivities and the main routes used for PPy/conducting composite synthesis, respectively.

Table 4. Summary of Materials and Conductivities of PPy/Wood Derived Materials Composites *

Polymerisation technique	Wood derived material	Oxidant and temperature	Conductivity S/cm	Ref.
Py polymerisation on individual fibres/particles	Wood sawdust	APS, room	0.32	Sapurina et al. 2005
	BKS	$FeCl_3$, 0°C	(20 Ω/cm^2)	Ding et al. 2010a
	BKS	$FeCl_3$, APS, room	0.26	Kelly et al. 2007
	BKS, TMP	$FeCl_3$, 0°C	0.1	Huang and Ni 2006
	BSK	$FeCl_3$, 0°C	(1.2 Ω/cm^2)	Ding et al. 2010
	Cotton yarn	$FeCl_3$, room	0.006	Hosseini and Pairovi 2005
Py polymerisation on paper sheets	Filter paper	$FeCl_3$, room	0.9	Bjorklund and Lundström 1984
	Filter paper	$FeCl_3$, APS	6	Johnston et al. 2005
	Pinus radiata	$FeCl_3$, APS	4.3	Richardson et al. 2006
	Cladophora cellulose mat	$FeCl_3$, room	2.2	Mihranyan et al. 2008
	MFC mat	$FeCl_3$, room	1.5	Nyström et al. 2010
Py polymerisation with conductivity enhancers	CMC	APS, 3°C	10.4	Sasso et al. 2010a
	Xylan	APS, 3°C	10.3	
	MFC	APS, 3°C	7.9	
	CMC	$FeCl_3$, room	0.8	Sasso et al. 2008
	LS	$FeCl_3$, room	0.08	
	LS	$FeCl_3$, 0°C	1.6	Yang and Liu 2009
	EHEC	$FeCl_3$, 2°C (water ethanol mixture)	7.3	Mandal and Mandal 1994
	MC	$FeCl_3$, 0°C	0.2	Bjorklund and Liedberg 1986
	HPC	$FeCl_3$, 0°C	0.2	Amaike and Yamamoto 2006
Py polymerization with wood derivatives for conducting films production	MFC	APS, 3°C	2.6	Sasso et al. 2010a
	CMC	APS, 3°C	0.08	
	CMC	APS, 3°C	0.11	Sasso et al. 2011
	Cellulose gel	KPS, room	~0.01	Rußler et al. 2011
	CLC	$FeCl_3$, -8°C	1.1	Yin et al. 2001
	CD	$FeCl_3$, 40°C	0.1	Li et al. 2006

* Abbreviations: EHEC is ethylhydroxyethylcellulose, MC is methylcellulose, LS is lignosulfonate, CLC is crosslinked cellulose, CD is cellulose diacetate, BKS is bleached Kraft softwood, TMP is thermomechanical pulp, MFC is microfibrillated cellulose, APS is ammonium peroxydisulfate, and KPS is potassium peroxydisulfate.

Since the main characteristics of actual PPy-wood derivatives composites (i.e. conductivity, tunable porosity, high specific surface area, flexibility, high mechanical resistance, and their elaboration via water-based processes) provide ways to cope with the ever increasing demand of new functional materials for flexible electronics, sensors, and energy storage devices, wood derivatives are attracting growing interest and further intensification of their study and use for, up to now, unconventional applications can be expected for the near future.
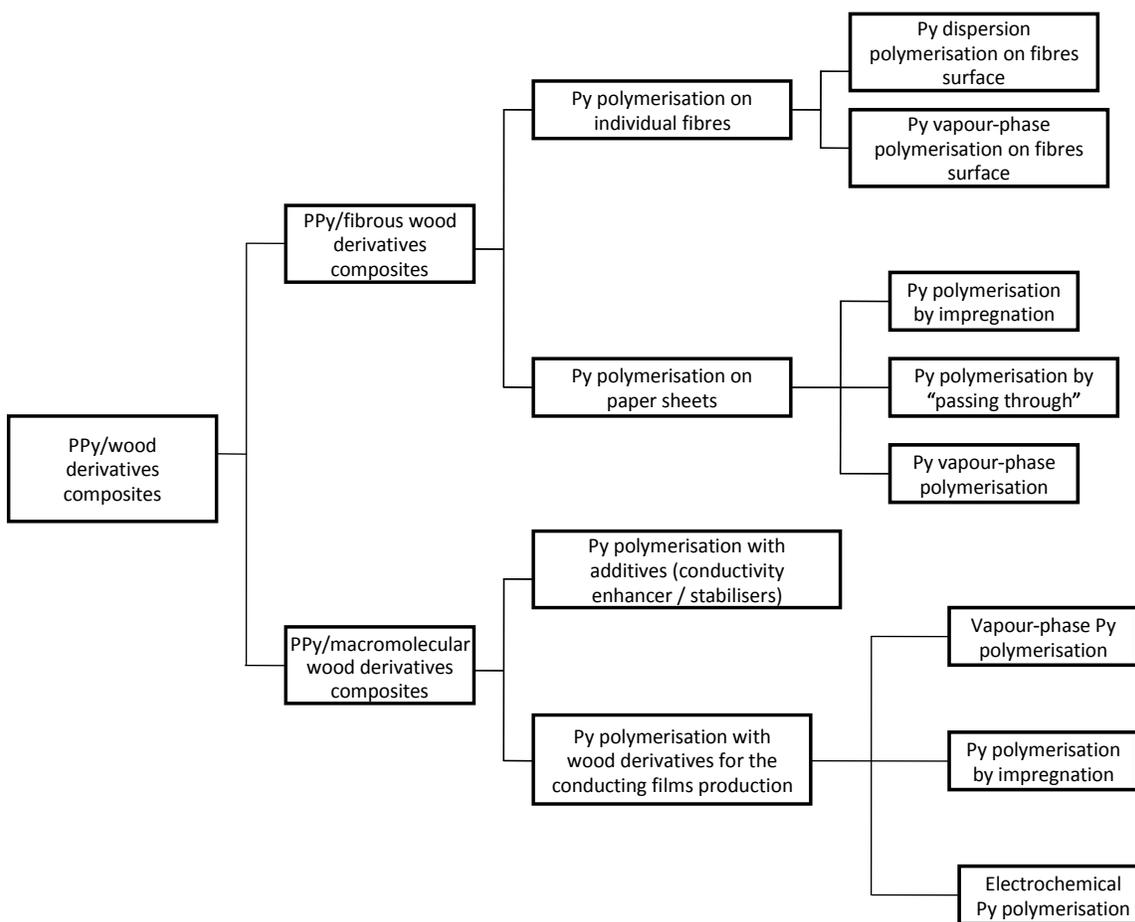
Fig. 16. Diagram of the Py polymerisation routes to obtain PPy/wood derivatives composites.

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