Macromol. Symp. ***189****, 83–103 (2002)*

Conductive Polymer Blends: Preparation, Properties and Applications

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Summary: This article presents a brief review concerning the production of conductive polymer blends and composites which combine conducting and insulating polymers. Different strategies for preparing these mixtures are examined, with emphasis on several properties of the final mixtures, such as: electronic conductivity, mechanical behaviour and thermal stability. The advantages of using blends in some technological applications instead of pure conducting polymers are discussed.

Historical Approach

After Shirakawa's pioneering work[1] showing that polymeric materials could exhibit reasonable electronic conductivity, the research in this field has developed intensely. Nowadays, organic polymers with intrinsic conductivity are a well-known and studied class of materials. Indeed, some conducting polymers are now being produced on a commercial scale by several industries.[2-5] Besides their intrinsic electrical conductivity, they also present electroactivity, electrochromism and semiconductor behaviour, which qualify them for several applications, such as: batteries[6], capacitors[7], electrochromic displays[8-10], field effect transistors [11,12], light emitting diodes[13], photovoltaic [14] and photoelectrochemical cells.[15-17]

Despite these interesting properties, the difficulty of processing conducting polymers by the usual methods of the polymer industry (extrusion, injection moulding, lamination, etc.) restricts their large scale use. Thus, several studies have focused on the synthesis of thermally processable conducting polymers.[18-21] Sulphonic acids, such as dodecylbenzenesulphonic and camphorsulphonic acids, are largely used to obtain polyaniline, PAni, with suitable mechanical properties.[22-25] However, the most

CCC 1022-1360/00/$ 17.50+.50/0

frequently used method to produce conductive materials with this property is by mixing conducting polymers with conventional processable polymers.[26]

The technology of producing polymer mixtures has become a very important route for obtaining new materials, by combining well-known polymers. Indeed, in recent decades this method has been more frequently used by the polymer industry than research and development on new polymeric materials.[27] The aim of making these mixtures, historically called *polymer blends*, is the synergistic combination of the properties of their components. With mixtures of electronically conductive and insulating polymers, the main objective is the preparation of polymeric materials with good rheological properties and processability associated with electronic conductivity, to produce conductive films for static charge dissipation or electromagnetic interference shielding applications.[28] Other properties inherent to conducting polymers, however, could be affected by the insulating matrix, such as electrochromism and redox behaviour. The field of producing conductive blends by mixing conducting and insulating polymers has been widely studied and several reviews discuss this subject.[29-31] The most commonly used polymers are polypyrrole, polyanilines and polythiophenes, because of their easy preparation and environmental stability.

Mixtures of insulating and conductive polymers are called *polymer blends* or *composites*, however, the latter name is more often used when the insulating polymer is basically a host matrix to the template synthesis of a conducting polymer. For this reason, in this article, the term *conductive blend* is used to designate all types of conductive polymer mixtures, independent of the miscibility between the components or the preparation method.

Conductive polymer blends were first prepared by the electrochemical polymerisation of pyrrole in a poly(vinyl chloride), PVC, modified platinum electrode.[32,33] A PVC film adherring to a platinum plate was swollen by the electrolyte solution containing the pyrrole monomer and, when a suitable potential was applied between this electrode and a reference electrode, anodic polymerisation started from the polymer | electrode interface and propagated to the polymer | electrolyte interface. The association of the electronic properties of the conducting phase with the mechanical properties of the insulating phase produced a new material with thermoplastic-like mechanical properties and electrical conductivity in the range of 10 to10^2 S cm^{-1}.

In another pioneering work, blends of polypyrrole, PPy, and PVC or brominated polyvinylcarbazole were prepared by potentiostatic polymerisation of pyrrole into the insulating films.[34] The product showed conductivity of 2 S cm^{-1} and 60 % transmittance at 633 nm. According to the authors, the bleached reduced blend was more stable than pure polypyrrole prepared under the same conditions. Nowadays, several other methods are used to prepare conductive blends. These have a significant effect on the final properties of the mixtures. In the follow section, a brief discussion of preparation methods is presented.

Preparation Methods

Electrochemical synthesis: the electrode coating method

As mentioned above, the electrochemical synthesis of a conducting polymer into an insulating film was the first method used to prepare a conductive polymer blend.[32,33] Basically, the working electrode is coated with an insulating polymer, which can be swollen by the electrolytic solvent, and, by the application of a suitable potential or current, the monomer polymerises into the matrix. For this preparation, a conventional electrochemical apparatus (potentiostat/galvanostat, three electrodes/one compartment electrochemical cell, electrodes and an electrolyte containing the monomer) is required. Since the working electrode is previously coated with the insulating film, this method is called the *Electrode coating method.*

Depending on the miscibility, the conducting polymer can be formed within the insulating matrix or between the electrode and the insulating film. The first result occurs if three conditions are fulfilled by the insulating matrix: (i) swelling by the solution containing the monomer and the electrolyte, (ii) a certain degree of miscibility with the conducting polymer and (iii) stability in the potential range used and in the electrolytic medium.

Initially, the electrode coating method was the most used alternative to produce conductive polymer blends.[35-39] Despite the possibility of large scale production of conductive films using a rotating-drum electrode [40], electrochemical methods are usually restricted to small-scale preparations and are presently used only in work related to technological applications where the conductive film must necessarily be deposited on conductive substrates.[41] Thus, the most recent work in this area describes preparation methods which enable large-scale production.

Chemical methods

In situ chemical polymerisation of the conducting polymer into an insulating film is very similar to electrochemical methods, but the potential needed to promote the formation of the conducting polymer is supplied by an oxidising agent. In comparison to electrochemical methods, the main advantage of this method is that the dimension of the conductive film is not limited by the electrode area.

Polymerisation can be achieved by adding the monomer to a solution containing the insulating polymer and an oxidising agent. Blend films are obtained by subsequent evaporation of the solvent. Nicho and Hu used this method to produce blends of PPy with poly(vinyl alcohol) and poly(vinyl acetate). These authors dispersed pyrrole in a solution containing the insulating matrix and ferric chloride. After solvent evaporation, the resulting films showed electronic conductivity of *ca.* 10^{-3} S cm^{-1} and good miscibility between the conductor and the insulating components.[42]

The final evaporation step can be eliminated if the oxidant is incorporated into an insulating film, with subsequent exposition of this film to vapours of the monomer. The solid inorganic oxidant can be introduced into the insulating film in several ways, including mechanical mixing and co-dissolution. Cupric chloride was first incorporated into ethylene-propylene-ethylidene norbonene terpolymer, EPDM, by calendering and the filled insulating films were exposed to pyrrole to obtain an EPDM-PPy blend.[43] Previous incorporation of the oxidant by co-dissolution was used by Mano and co-workers for preparing films by evaporating a tetrahydrofuran solution of PVC and ferric chloride with subsequent exposition to pyrrole vapours.[44]

Chemical polymerisation of the conducting polymer into the polymer matrix can also be done by including the monomer into the polymer matrix and subsequent exposition of the resulting film to an oxidising agent. Green-transparent and conductive mixtures of PAni/poly(methyl methacrylate), PMMA, and PAni/PVC were obtained by dissolving aniline and the host matrix in a common solvent and, after evaporation, immersing the resulting film in an aqueous ferric chloride solution.[45] In another work, Lee and Hong coated porous Nylon membranes by immersing them in a pyrrole solution, with the subsequent addition of a ferric chloride solution to the reaction medium.[46]

In chemical methods, one of the reactants, the monomer or the oxidant, is first added to the insulating host matrix. Thus, the polymerisation kinetics for the conducting polymer depend on the diffusion coefficient of the second reactant into the insulating host. Also, formation of the conducting polymer near the surface of the insulating host may preclude further diffusion of the reactant into its bulk, leading to more heterogeneous systems.

Mechanical methods

Research in the field of conducting polymers has attracted great interest because of the several technological applications proposed for these materials. However, the conducting polymers initially developed were highly infusible and insoluble, restricting their use on a large scale. Great effort was devoted to solve this problem and the statement that polyaniline could be melt-processable and soluble in some solvents by using organic acids as dopants[22-24] increased the possibilities of producing conductive polymer blends by different methods. Soluble polyanilines may also be obtained by polymerising *ortho* substituted anilines.[47-49] For these reasons, polyaniline and its derivatives are the conductive polymers most frequently used to prepare conductive blends by the mechanical mixture of the blend components.

Blend components can be mixed by two methods: (i) using the common machinery of the plastics industry, such as a double screw counter-rotating mixer or a double-screw extruder, and (ii) by co-dissolution. The conducting polymer used in these methods is usually obtained by chemical synthesis, because a larger amount of material can be produced by this route.

Co-dissolution means dissolving the polymeric components in a common solvent and evaporating or spinning the resulting mixture over a suitable substrate to obtain a film. In general, undoped (deprotonated) polyanilines are more soluble than the parent protonated polyaniline, and an alternative to produce conductive blends is to dissolve the emeraldine base and the polymer host in a solvent. After solvent evaporation, the blend film is exposed to vapours of an acid dopant. Attempts have also been carried out to obtain polymer blends from doped polyanilines.

A systematic study about the solubility of polyaniline and some of its alkoxy-substituted derivatives showed that the acid dopant has a strong influence on the solubility of these polymers in several solvents.[50] In this sense, polyanilines doped with camphor sulphonic acid, PAni-CSA, and with dodecylbenzenesulphonic acid, PAnis-DBSA, are soluble in different solvents and blends of this polymer with several thermoplastics and elastomers have been prepared by co-dissolution in *m*-cresol[51] or chloroform.[51-54]

Poly(*o*-methoxyaniline) doped with different acids is highly soluble in dimethylformamide, DMF, and blends of this polymer with polyurethane[55], polyacrylonitrile[56] and poly(ethylene oxide-*co*-epichlorohydrin)[57] were prepared by co-dissolution of the polymers in DMF.

The co-dissolution method can also be used to obtain conductive fibres. Norris and co-workers dissolved poly(ethylene oxide) and PAni-CSA in chloroform and ultrafine conductive fibres, with diameters less than 2 μm, were produced by electrostatic spinning.[53]

In a recent work, Ahmed and co-workers[58] showed that specific substances may act as both solvent and dopant for the conducting polymer. These authors dissolved undoped poly(*o*-toluidine)/poly(*m*-toluidine) and PMMA in formic acid and obtained a thermoplastic blend containing the conducting polymer in its protonated form. The same strategy was also used with aqueous methanesulphonic acid (70 % by wt) to produce a blend of PAni and poly(4-vinyl pyridine).

As stated above, co-dissolution is one of the most widely used methods to prepare conductive films based on polyanilines. By this method it is possible to produce films with larger dimensions than using *in situ* electrochemical or chemical methods. However, solvent evaporation of large-areas films is not a suitable method to produce conductive blends on a commercial scale. For these applications, mechanical mixing of the polymers by the conventional machinery present in the polymer industries is preferred.

From the industrial point of view, a thermally processable conducting polymer must present the following properties: (i) appropriate rheological parameters at the temperatures typically used for the host insulating matrix; and (ii) no changes in its electronic conductivity with thermal degradation.[20]

Thermoplastic conductive polymer blends of PAni and a series of insulating hosts (PVC[3,20,59], polyethylene[3], polypropylene[3], polystyrene[3], Noryl™[60] and poly(ethylene terephtalate)[60]) have been produced by different thermal processing methods, ranging from miniature extruders[3], Brabender mixers[59], Rheometers equipped a counter-rotating mixer[60] and hot pressure[61], to pilot-plant scale production.[3]

Elastomeric conductive blends have also been produced by mechanical processing. Vallim and co-workers mixed PAni and nitrilic rubber by calendering and produced elastomeric films by vulcanising the rubber under heating and pressure.[62] EPDM and PAni were mixed in an internal counter-rotating mixer coupled to a Torque Rheometer and the resulting mixture was vulcanised under heat and pressure to obtain conductive films.[63,64]

Mixing temperature, design of the screw and rotating speed are some variables which must be adjusted to blend polymers. Temperature should permit a good flow of the molten polymers, but remain low enough to prevent thermal degradation of the components. The design of the screw should provide the shortest possible residence time. Rotation of mixer blades or the extruder screw must be adjusted to induce good mixing and avoid degradation by shearing.

Mechanical mixing of the blend components is the best alternative to produce conductive blend films on a large-scale. The recent progress achieved in obtaining melt-processable conducting polymers, which can be extruded, mixed or pressed by ordinary machinery present in the polymer industries, makes possible their real utilisation as raw-material for producing conductive flexible films for several technological applications.

Other methods

Lack of solubility is not a problem in preparing conductive blends: an adaptation of the co-dissolution method was recently proposed by Haba and co-workers, who prepared blends of PAni doped with dodecylbenzenesulphonic acid, DBSA, by mixing aqueous dispersions of PAni-DBSA and several insulating hosts, with the subsequent evaporation of water.[65] In a similar way, Gospodinova and co-workers prepared a highly conductive and transparent polymer blend by dispersing very fine colloidal particles of PAni in a poly(vinyl alcohol) solution.[66]

As discussed above, several routes exist to prepare conductive polymer blends. The choice of using one methodology instead of another must take into account the final properties of the resulting mixtures. Conducting polymers and insulating matrixes are usually imiscible or partially miscible. Complete miscibility is undesirable because the conductive network needed to promote the conductivity is not formed if this situation occurs. For the same components, different methods lead to mixtures with. different degrees of compatibilization. However, all methods lead to the formation of mixtures with the necessary compatibilization to produce free-standing films.

Also, the preparation method should be chosen by taking into account the applications where the blend will be used. For example, *in situ* electrochemical polymerisation is usually preferred in technological applications where a modified electrode is required, mechanical methods are preferred if large-scale production of conductive films are needed.

Properties: conductivity, mechanical behaviour and thermal stability

Electronic conductivity

The first objective of adding a conducting polymer to an insulating host is to increase the electronic conductivity of the host. For the production of conductive films, the conducting polymer content needs to reach the percolation threshold to cause the onset of electronic conductivity. This concentration limit is markedly lower than that observed with inorganic-filled insulating polymers. According to theoretical studies, this situation occurs when the conductive filler represents 16 % (v/v) in the mixture [67]. Several examples of conductive polymer blends show the low percolation threshold achieved by using conducting polymers.[68-70] Flexible conductive films prepared by casting a DMF solution containing poly(*o*-methoxyaniline) doped with *p*-toluenesulphonic acid, PoAnis-TSA, and poly(ethylene oxide-*co*-epichlorohydrin) presented the onset of the conductivity with *ca.* 2 % (v/v) of the conducting polymer.[57]

Yoon and co-workers[71] demonstrated that, for the system PMMA/PAni, it is possible to produce a fibrilar network of the conducting polymer when adding 0.5 % (v/v) of polyaniline to the insulating matrix. The authors interpreted the low percolation threshold in terms of the formation of an interpenetrating network between the components of the mixture.

Conductive polymer blends with ultra-low percolation thresholds have also been produced. Juvin and co-workers described the preparation of a blend by mixing PAni-CSA, PMMA and a plasticiser, obtaining a percolation threshold of 0.041 wt%.[72] In another work, Fraisse and co-workers produced a conductive polymer blend where the addition of 0.03 % by weight of conducting polymer to the insulating matrix promoted the onset of electrical conductivity.[73]

Recent advances in this area are leading to the preparation of highly conductive films, mainly based on polyaniline blends. Yang and Lee added only 5 wt % of polyaniline to a water soluble polyurethane and observed an electrical conductivity of 5 S cm^{-1}.[74] Barra and co-workers[75] obtained conductivity values of 1 S cm^{-1} in blends of polyaniline doped with dodecylbenzenesulphonic acid, PAni-DBSA and poly(ethylene-

co-vinyl acetate), EVA. According to the authors, the protonation degree of the conducting polymer is more effective in the mixture than in pure polyaniline. In another recent work, Makela and co-workers achieved 10 S cm^{-1} with a blend of PMMA and PAni-CSA, containing 40 wt % of the conducting polymer.[76]

Hopkins and Reynolds[77] observed that, for mixtures of polyaniline and amorphous or crystalline Nylon-6, the electrical conductivity is 10 times higher in blends using crystalline polyamide (1 S cm^{-1}, for the blend containing 10 wt% of polyaniline). The authors associated these interesting results to the formation of more organised conductive pathways in the blend containing the crystalline host. This important feature opens the possibility of producing films with very high conductivity.

The electronic conductivity observed in a polymer blend is usually lower than that observed for the pure conducting polymer used to product this blend. However, Han and Im described, in an interesting work, that sometimes it is possible to increase the conductivity by producing a polymer blend.[78] These authors observed that the electronic conductivity of a polymer blend composed of PAni-CSA and a polyimide is higher than that observed for the pure polyaniline doped with the same acid. According to the authors, this effect results from the annealing of polyaniline chains, induced by the insulating matrix.

Mechanical properties

As mentioned, the aim of making conductive polymer blends is to combine the electronic properties of the conducting polymers with the mechanical properties of the insulating polymers. Compared to the pure conducting polymers, blends always present enhanced mechanical properties. However, compared to thermoplastics or elastomers, conductive polymer blends often show loss of thermoplastic/elastomeric behaviour. This undesirable effect is usually proportional to the conducting polymer content in the mixture.

Depending on the conducting phase content, the mechanical properties of the insulating host can be retained. Mixtures of poly(ethylene oxide-*co*-epichlorohydrin) and PoAnis-TSA containing 10 wt% of conducting polymer showed Young moduli and elongations at break similar to those observed for the pure host.[57] This behaviour was also observed in blends of EPDM and polyaniline containing the same concentration of conductive polymer.[63] An interesting phenomenon observed in elastomeric conductive blends is the reinforcing effect induced by the conductive phase in the elastomer.[62] This effect was observed for EPDM-PAni blends and, after hot pressing without a vulcanising agent, the presence of the conducting polymer inhibited elastomer solubilisation and produced a cross-linked rubber.[64] On the other hand, Faez and De Paoli, in a recent work, showed that processing PAni-DBSA in an internal mixer with a small concentration of EPDM rubber produces a plasticized conducting polymer, which can be laminated into highly conductive and elastic films.[79]

Progress in maintaining the mechanical properties of the insulating host are also achieved in thermoplastic blends. Pioneering work on PVC/polypyrrole blends stated that flexible films were obtained, but stress-strain curves of the mixtures showed that the PVC mechanical behaviour was changed by adding the conducting polymer.[33] However, a mixture of high density polyethylene, HDPE, and PAni-DBSA showed that it is possible to retain the mechanical properties of the thermoplastic after the addition of an small concentration of PAni-DBSA.[3]

Highly conductive films are usually obtained in mixtures containing high contents of conducting polymers and it is hard task to maintain the mechanical properties of the insulating host with this addition. However, the mechanical behaviours of these mixtures are always superior to those observed for the pure conducting polymers. Besides, it was shown that the conducting polymer content needed to reach the percolation threshold to cause the onset of electronic conductivity is low. In addition, low contents of conducting polymers may be added to both elastomers and thermoplastics with no changes in the mechanical behaviour of the insulating hosts.

Thermal stability

An additional effect of adding a conducting polymer to an insulating matrix is the increase of the thermal stability of the latter. Large-scale methods for producing conductive blends involve processing at higher temperatures. Hence, the thermal stability of the components is crucial to obtain mixtures with high performances.

Thermogravimetric analysis of conductive blends based on PoAnis-TSA showed that, depending on the proportion between the components, the conducting polymer retards the degradation processes of the insulating matrix.[80] Figure 1 compares the thermal degradation process of several blends of this conducting polymer and poly(acrylonitrile-*co*-vinyl acetate), P(AN-VA), with theoretical curves estimated from the averages of the curves related to the pure polymers.

Peaks I, III and IV in Figure 1 are related to the degradation processes of the insulating matrix: (I) acetic acid liberation, (III) –CN scission and HCN liberation, (IV) cyclisation/crosslinking processes. In the mixtures, -CN scission of P(AN-VA) is less intense than expected (dotted curves), showing that the addition of PoAnis-TSA retards this process. This effect was attributed to the acid-acceptor behaviour of the conducting polymer. Probably, PoAnis-TSA interacts with the insulating matrix, via its non-protonated nitrogen atoms and dipoles formed in the P(AN-VA) chains, during the first step of the -CN scission process.

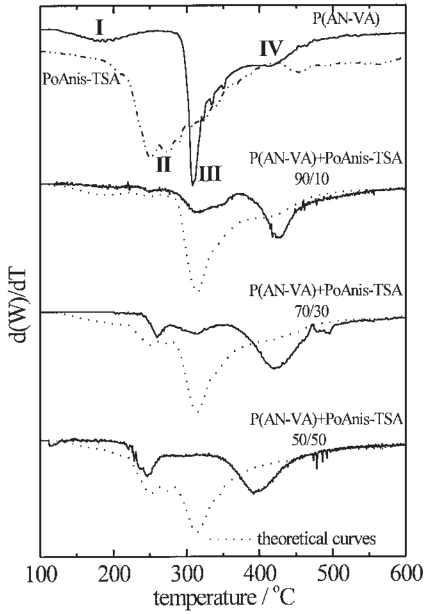

Figure 1 – 1st derivative TG curves of (–) pure P(AN-VA), (-..-..) pure PoAnis-TSA and blends containing different proportions between the components. Dotted lines correspond to the curves expected if no interaction occurs between the polymers. Copyright by Elsevier Science.[80]

Applications

Typical technological applications for conductive polymer blends include all kinds of systems based on pure conducting polymers. Small-scale electrochemical preparations are indicated for using in electrochemical devices, such as displays, smart windows, batteries and capacitors. In addition, large-scale preparation methods permit the production of conductive films with dimensions and mechanical properties adequate to be used in anti-static coatings, anticorrosive protection and electromagnetic shielding. Indeed, the use of conductive blends in some applications, instead of pure conducting polymers, leads to systems with optimised performances.

Conductive films for EMI shielding and corrosion protection

The increasing electromagnetic pollution, inherent in the use of electronic, computing and telecommunication equipment, and the not well-established effects of this electromagnetic interference (EMI) on human health are very relevant arguments in the modern World. Besides, perturbations from EMI also affect the operation of electronic systems, leading to malfunction or even failure of these devices.[81]

The approach of using conductive polymer blends, instead of inorganic-filled polymers, for this purpose is very interesting, because large amounts of metal/inorganic fillers are required to achieve reasonable EMI shielding, drastically affecting the mechanical properties of the mixtures. In fact, this was one of the first applications envisaged for conductive polymers.[82]

The first results of Taka[28], showing that blends of poly(3-octylthiophene) with several insulating thermoplastics (PVC, EVA and polystyrene) present reasonable EMI shielding effectiveness, encouraged the research in this field. For defence purposes, a large frequency range should be covered. Surface deposition of polypyrrole on PVC produced mixtures with microwave absorption from 0.1 to 20 GHz.[83] Mixtures of PAni and acrylonitrile-butadiene-styrene terpolymer, ABS, achieved shielding effectiveness of 60 dB at 101 GHz, with 50 wt% polyaniline.[84] The possibility of producing conductive films with suitable mechanical properties has stimulated research on the use of blends as EMI shielding materials and numerous examples can be found in the literature.[28,81-86]

Conducting polymers are also efficient to avoid metallic corrosion due to their unique redox properties. The mixture of these polymers with a suitable insulating matrix may lead to the production of very promising coatings for anti-corrosion purposes. The use of a mixture of PAni-CSA and epoxy resin to protect mild steel from an acid solution reduced the redox current by about five orders of magnitude and produced a 500 mV shift of the corrosion potential to the noble direction.[87] In another work, the same authors used blends based on both emeraldine base and HCl-doped PAni for the same purpose.[88]

Conductive films may also be used in a series of other protective coatings, such as marine antifouling agents[89] and electrostatic dissipation.[84]

Photolithography

Novel methods using photolithography to fabricate patterned electroactive films in highly specific microstructures are being extensively studied. Bidimensional structured patterns with micrometer and submicrometer spatial resolution can be achieved with this technique. Electroactive monomers that can be photopolymerised, and polymers that can be photocrosslinked or doped, can be used to fabricate microstructured electroactive polymer films adsorbed on optically transparent and conductive substrates.[90] The applications of such technology include individually addressable, pixel-sized devices that could be used to fabricate television-like screens.[91]

Some specific mixtures of conducting and insulating polymers have interesting properties for micrometer patternings. It is well known that PVC and other chlorinated polymers liberate hydrochloric acid under some conditions, such as UV, high energy irradiation or heating.[92] Otherwise, polyaniline changes its properties by acid doping/dedoping.

Emeraldine base blends with poly(vinylidene chloride-*co*-vinyl acetate) or PVC showed strong colour variations and conductivity increases by exposure to UV irradiation,[93] γ-radiation or e-beams.[94] These changes have been assigned to the dehydrochlorination of the polymer host and the doping of the emeraldine base by the HCl generated *in situ*. Taking into account that emeraldine base is significantly more soluble in several solvents than the parent HCl-doped PAni, this process can be used to produce lithographic patterns. Using a synchrotron source, Carinhana and co-workers irradiated a PVC/PAni base film and obtained patterns with micrometer resolution, as shown in Figure 2.[95]

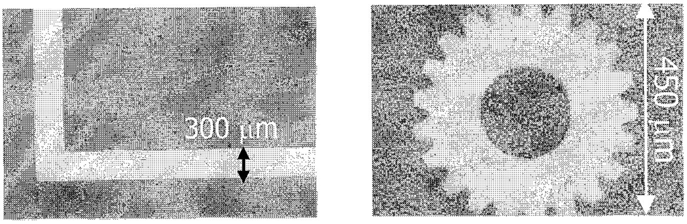

Figure 2 - Lithographic patterns recorded with PAni-PVC films. Bright coloration corresponds to irradiation exposed areas. Copyright by John Wiley & Sons.[95]

Electrochromic devices

Electrochromic displays are another typical application for conducting polymers, in which better performances may be achieved if the pure polymer is replaced by a conductive polymer blend. For smart window applications, it is convenient to make flexible devices to permit coating of pre-existing windows. The use of conductive polymer blends with improved mechanical properties as electrochromic materials in such devices permits the construction of flexible systems, avoiding possible ruptures in the active films.[96]

Electrochromic properties and device stability are also optimised if a conductive blend is used. Figure 3 shows the optical contrast at 620 nm of the two elastomeric blends: (i) poly(ethylene oxide-*co*-epichlorohydrin)/poly(N,N-dimethylbipyrrole),Poly(NNDMBP), and (ii) poly(ethylene oxide-*co*-epichlorohydrin)/poly(4,4'-dipentoxy-2,2'-bithiophene), poly(ET2), in a liquid electrolyte.[96]

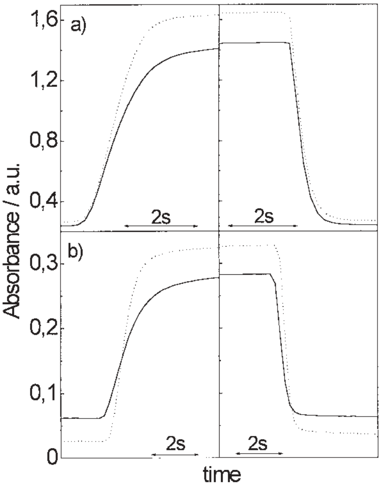

Figure 3 - Optical responses at 620 nm for colouring and bleaching steps. a) Poly(ET2), b) Poly(NNDMBP). Full lines: pure conducting polymers, dotted lines: blend materials. Copyright by Wiley-VCH.[96]

Both blends present higher chromatic contrast and faster colouring/bleaching kinetics than the pure conducting polymers. The elastomer was used in both blends because it is a good ionic conductor when mixed into inorganic salts.[97] The results were assigned to morphologic changes in the conducting polymer phase induced by the insulating host. Indeed, Amanokura and co-workers showed that interfacial transport is higher in a polypyrrole/polymer electrolyte blend than in the pure polypyrrole.[41]

Figure 4 compares the optical contrast at 620 nm for electrochromic devices based on these blends as a function of the colouring/bleaching cycles. It is clear that the device based on the elastomeric blends shows a longer lifetime than that based on the pure polymers. The presence of the insulating host probably precludes crosslinking reactions between the chains of the conducting polymer and improves the device performance.

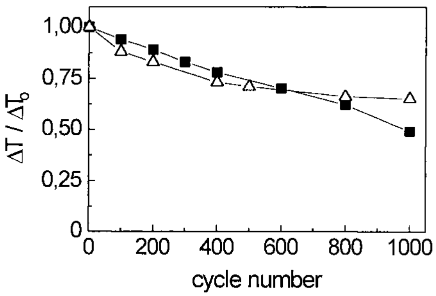

Figure 4 - Optical contrast of electrochromic devices at 620 nm as a function of the number of double potential steps: (Δ) using blend materials, (■) using pure poly(ET2) or poly(NNDMBP). Copyright by Wiley-VCH.[96]

Photovoltaic cells

The great demand for energy, associated with the limited resources of traditional fuels and environmental problems, has led to intensive research on the conversion of solar energy to electricity. Solar light is the most important source of energy and represents mankind's only inexhaustible energy source. One of the most promising tools to make use of solar energy is its direct conversion into electrical energy using photovoltaic or photoelectrochemical cells.[98]

These cells represent another good example of how conductive polymer blends may optimise the properties inherent to conducting polymers. Bulk donor-acceptor heterojunctions between conducting polymers and fullerenes have been used for photovoltaic devices with suitable energy conversion efficiency (around 0.04%).[99] By mixing a poly(*p*-phenylene-vinylene) derivative, PPV, a methane fullerene and polystyrene, Brabec and co-workers obtained an heterojunction with monochromatic power conversion efficiency of 1.5%.[100]

An improvement of the photoelectrochemical properties of PAni was observed by Neves and De Paoli for PAni supported in a microporous cellulose acetate (CA) membrane .[101] Figure 5 compares the photoelectrochemical responses of a pure PAni film and a CA/PAni film. It is noteworthy that the polymerisation of aniline in the pores of the cellulose acetate membrane intensifies the photoelectrochemical response of the polymer.

According to the authors, the insulating host permits a higher swelling of the photoactive material with the electrolyte solution containing a redox couple and favours the diffusion processes in the polymer | electrolyte interface. Also, the spongy-like structure of the membrane permits a deeper penetration of light, producing a more intense photoeffect.

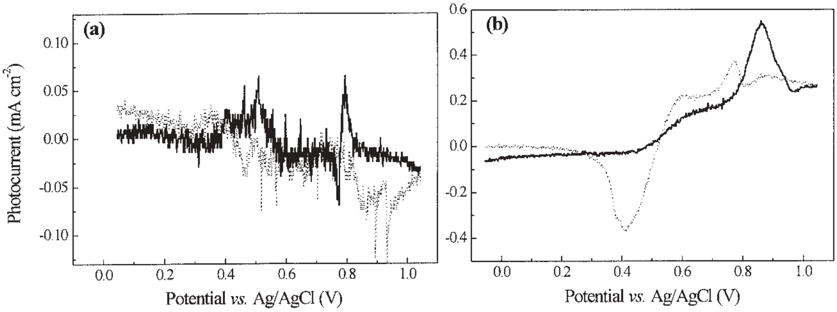

Figure 5 – Differential cyclic voltammetry for (a) pure PAni, (b) CA/PAni blend. Copyright by Elsevier Science.[101]

Light-emitting electrochemical cells

Light emitting diodes, LED, are the reverse of photovoltaic cells: while in the latter the light is used to produce an electric current, in LED a potential difference is applied to produce light. Taking into account the hole-injecting properties of the conducting polymers under an applied potential or current, flexible light emitting diodes based on these materials were first proposed by Burroughs and co-workers, generating great interest in the research of the so-called “polymer LED”, also called OLED.[13]

A problem to be solved to achieve high efficiency in polymer LED is the preponderance of hole injection over electron injection, because metals with a sufficiently low work function necessary for the correct operation of these devices are chemically reactive. Besides, the faster mobility of holes in comparison to electrons also promotes a decrease in the device efficiency.

An alternative to avoid these difficulties are the *light-emitting electrochemical cells*, LEC's, first described by Heeger and co-workers in 1995.[102] LEC's are based on the characteristic of both p- and n-type doping of conducting polymers. A schematic representation of a LEC is shown in Figure 6, where the electroluminescent layer is composed of a blend of an electroluminescent polymer with a polymeric electrolyte. The electrolyte is needed to provide ions for the occurrence of both p- and n- doping in the polymer. Among the polymer electrolytes, the most used for LEC applications is the polymer complex composed by poly(ethylene oxide), PEO, and a lithium salt.[102,103]

By applying sufficiently high voltage between the metallic contacts, cations and anions move in opposite directions. The polymer side adjacent to the anode is oxidised and p-type carriers are introduced, while the polymer side closer to the cathode is reduced and n-type carriers are introduced. Electrochemical doping occurs when the applied potential is higher than the energy gap of the polymer. [104,105]

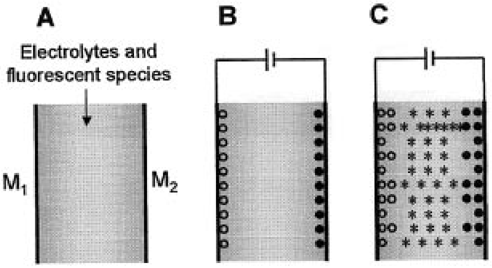

Figure 6 - Schematic representation of the electrochemical processes in a LEC. Electrodes are named M_1 and M_2, (o) is the oxidized species, (•) are the reduced species and (*) are the neutral electron-hole pairs. (A) The cell under zero bias, (B) Doping opposite sides as n- and p-types, (C) Charge migration and radiative decay. Copyright by AAAS.[102]

The charge balance in this process is provided by cation and anion mobility into the blend. As a consequence, a p-n junction is created in the bulk of the polymer film, where recombination processes and decay occur with light emission.

An interesting example of LEC was reported by Yang and Pei, who separately blended PPV and poly[(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene)], MEH-PPV, with an electrolyte consisting of PEO and a lithium salt.[106] The configuration of the electrochemical cell was Al | MEH-PPV blend | PPV blend | ITO and it showed red-orange emission under forward bias and green emission under reverse bias. According to the authors, a p-n junction is formed closer to the cathode due to the asymmetry of electron-hole injection and transport. Thus, the LEC emits red-orange light from the MEH-PPV layer when this side is charged negatively and emits green light from PPV when the PPV blend is charged negatively.

To enhance the performance of the LEC, Cao and co-workers included several liquid additives to the electroluminescent layer based on MEH-PPV + PEO + Li salt, to provide better compatibilisation between the components of the electroluminescent blend. [107] The surfactant-like behaviour of the additives causes a high surface area bicontinuous three-dimensional network morphology. The resulting LEC has better performance in comparison to the parent LEC without additive: the brightness increases from 10 to 1000 cd m^2. Besides, the additive-contaning LEC presents an efficiency of 2.5 %, which is similar to that obtained for a LED-type device using the same electroluminescent polymer.

Conclusions

The methods and results described indicate the variety of alternatives used to prepare conductive polymer blends. These mixtures have the typical applications envisaged for intrinsically conducting polymers. However, in some cases the resulting product has optimised properties in comparison to the pure conducting polymer. In addition, large-scale preparation methods (calendering, melt-mixing or extrusion) produce materials which can be used in other areas, such as EMI shielding.

The research on new conductive polymer blends has always aimed towards the production of processable materials. Although new low-cost preparation methods are still needed, large investments in this area reflect the interest and the optimism of chemists and technologists in obtaining new materials to fill several unexplored application niches.

Acknowledgements: The authors thank CNPq for research fellowships. WAG acknowledges the financial support from FAPERJ (E-26/170.096/2001) and CNPq (300149/2001-8). MAP acknowledges financial support from FAPESP (96/09983-0) and CNPq/PRONEx.

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