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Electroactive blends of poly(vinylidene fluoride) and polyaniline derivatives

Luiz F. Malmonge
Universidade Estadual Júlio de Mesquita Filho-UNESP, Depto. de Ciências, CP 31, Ilha Solteira, 15378-000 São Paulo, Brazil

and Luiz H. C. Mattoso*
Instituto de Física e Química de São Carlos, DFCM/USP, CP 369, São Carlos, 13560-970 São Paulo, Brazil
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The conditions for processing and doping of blends of poly(*o*-alkoxyaniline)s and poly(vinylidene fluoride) were investigated. Flexible, free-standing and stretchable films of blends of various compositions were obtained by casting. A low percolation threshold was observed with the onset of conductivity at low polyalkoxyaniline contents (i.e. 5%). Interestingly, these blends displayed electrochromism with colour changes similar to those of the parent conducting polymer, as observed from cyclic voltammetry measurements. This behaviour is seen even for low contents of the conducting polymer, indicating that a continuous conducting pathway, which is capable of exchanging charge, is formed within the insulating matrix.

(Keywords: polyaniline; blends; electrochemical response)

INTRODUCTION

The processibility of conducting polymers has been a crucial factor in making use of their interesting electrical and electrochemical properties in real applications[1–3]. The recent discovery that polyanilines could be processed from solution in the form of films[4] and fibres[5] has been a landmark in this respect. It has also been demonstrated[6–11] that polyanilines can be blended with a number of conventional polymers, thus leading to materials with high electrical conductivity and high mechanical strength. This certainly enhances the commercial viability of these conducting polymers.

The properties of polymeric materials, in general, are greatly affected by the method and conditions used for their processing. For a conducting polymer, an additional important variable, namely polymer doping, might also influence its final properties. In this work, we investigate the conditions employed for the processing and doping of blends of polyanilines and poly(vinylidene fluoride) (PVDF), and their properties. Because PVDF is a polymer with great potential[12–15] in the insulating industry, attention is given to the two regimes of conduction: (i) above the percolation threshold, where PVDF is expected to enhance the mechanical properties of the conducting polymer with only a minor loss in electrical conductivity, and (ii) below this threshold, where a small polyaniline content may increase the dielectric constant of the blend as a result of phase polarization.

EXPERIMENTAL

Polymer syntheses

The parent polyaniline (PANI), poly(*o*-methoxyaniline) (POMA) and poly(*o*-ethoxyaniline) (POEA) were chemically synthesized by using ammonium peroxydisulfate in aqueous 1.0 M HCl at 0°C, as described elsewhere[16]. The monomer to oxidant ratio was 4:1. The syntheses were terminated by filtering and washing the precipitated polymer with 1.0 M HCl. Polyalkoxyanilines with high conductivities were obtained by carrying out these washing procedures using acetone, (see ref. 17), instead of HCl. Dedoping was performed by treatment with 0.1 M ammonium hydroxide for 16 h at room temperature, to yield polyanilines in the emeraldine base form. Protonic doping of the dedoped polymers in the powder form was carried out by exposing them to 1.0 M aqueous acid solutions. (Hydrochloric acid (HCl), trifluoracetic acid (TFA), and toluenesulfonic acid (TSA) were used.) The resulting polymers were dried under vacuum for 24 h at room temperature. Poly(vinylidene fluoride) (Foraflon 4000 HD) was purchased from Atochem and was used as received.

Preparation of blends

Stock solutions of the conducting polymer (2% wt/vol) and PVDF (10% wt/vol) were prepared separately. No detectable insoluble fraction was noticeable upon filtering the solutions. These solutions were then mixed in several different proportions in order to obtain the desired blend composition. Films (15–30 μm thick) were prepared by casting the blend solutions onto a preheated glass slide,

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*To whom correspondence should be addressed which was then placed in an oven (70°C) with air circulation. The evaporation time varied from 1 to 10 h depending on the solvent used.

Characterization

The solubility of polyaniline and its derivatives, in both the undoped and doped forms, has been examined in *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, *N*,*N*-dimethylformamide (DMF), dimethylacetamide (DMA), chloroform and water. Polymers were doped with three different types of acid (HCl, TFA, TSA). The u.v.-vis. spectra of the polymers in DMF solutions were obtained by using a Varian spectrophotometer (Cary model 2315). The relative viscosity of the polymer dissolved in DMF (3.3 mg ml^{-1}) was determined in a Cannon–Ubbelohde viscometer, with measurements being taken for different doping levels of the conducting polymer. The same volume of acid which was used to dope the polymer was added to pure DMF for calibration purposes in each viscosity measurement. Electrical conductivities were measured by the standard four-probe method[18], while dielectric constant measurements were carried out on a capacitance bridge (General Radio Co.) at a frequency of 1 kHz. X-ray diffraction patterns were taken on a Rigaku RU-200B diffractometer, using Cu Kα radiation and a Ni filter. When stretched films were required, these were obtained by zone drawing[19] at $\sim$70°C.

The electrochemical responses of the various polymers were measured by cyclic voltammetry in an EG and G (PARC 273) potentiostat/galvanostat, using a standard three-electrode configuration involving a saturated calomel electrode (SCE). The blends were deposited on the gold working electrode by casting from DMF solutions. Films were cycled between -0.2 and 0.8 V (SCE), at a scan rate of 50 mV s^{-1}, in aqueous 1.0 M TFA.

RESULTS AND DISCUSSION

Solubility and preparation of polyblends

The solubility data shown in *Table 1* reveal that the poly(*o*-alkoxyaniline)s (POAAs) are indeed much more soluble in organic solvents than the parent polyaniline, especially when they are doped with conventional acids such as HCl and TFA. For example, POAAs in the undoped state are also soluble in low boiling point solvents such as chloroform. Moreover, they remain soluble in several other organic solvents (see *Table 1*) when doped with conventional acids (HCl or TFA), which is not the case for the parent polyaniline. It is remarkable that these derivatives have been found to be soluble even in water when doped with HCl. The high solubility of polyalkoxyanilines in both chloroform and water has recently made it possible to fabricate ultra-thin films via the Langmuir–Blodgett[20] and the molecular self-assembly[21] techniques, respectively.

These polyaniline derivatives are also soluble when doped with functionalized acids (e.g. TSA), where the counter-ion induces processibility, as recently discovered for the parent polymer[9]. These types of acid promoted gelation[22] for the parent polyaniline (in a few seconds after the preparation of, e.g. a 2 wt% solution), but not for the substituted polyanilines (see *Table 1*), probably due to steric effects. In addition, in some cases (marked with (d) in *Table 1*) the emeraldine base polymer could also be doped after dissolution by adding acid to achieve the desired doping level, which makes it possible to readily cast films in the doped state. This has allowed us to prepare blends with different types of polymer, some of which are described in this paper.

Films of polyblends could be obtained in the doped form using three different doping methods: (i) doping the polymer in the powder form before its dissolution, (ii) first dissolving the undoped polymer and then doping it by adding concentrated acid to the solution, and (iii) doping the blend, in the form of a film, by the conventional method (1.0 M aqueous TFA for 24 h).

In addition, blends of PVDF/POMA and PVDF/POEA could be prepared by making use of three co-solvents, namely, NMP, DMA and DMF. Significantly, doped polyalkoxyanilines were soluble in these solvents only when doped with TFA, but not with HCl. Although DMA and NMP could be used to prepare these blends, they usually lead to films with lower conductivities than those prepared with DMF. For this reason, therefore, DMF was the solvent chosen for further studies.

Figure 1 shows the u.v.-vis. spectra of POMA in DMF solutions using two different doping techniques (methods (i) and (ii), as described above). Two absorption maxima

Table 1 Solubility data of polyanilines and PVDF[a]

Polymer	Dopant	NMP	*m*-Cresol	DMF	DMA	CH$_3$Cl	Water[b]
PVDF	–	S	N	S	S	N	N
PANI	EB[c]	S	S	P	P	N	N
	HCl	N	N[d]	N	N	N	N
	TFA	N[d]	N[d]	N	N	N	N
	TSA	N[d,e]	N[d,e]	N	N	N	N
POMA/POEA	EB[c]	S	S	S	S	S	N
	HCl	N	S	N	N	N[d]	S
	TFA	S	S	S	S	N[d]	N
	TSA	S	S	S	S	N[d]	N

[a] The polymers were dissolved at room temperature, except for PVDF, where the solutions were heated to 70°C: S=soluble; N=not soluble; P=partially soluble

[b] The polymer must be wet with acetone or acetonitrile before solubilization

[c] EB=emeraldine base

[d] The solution of the undoped polymer can be doped by the addition of the specified acid

[e] The solution ($\sim$2 wt%) gels in a few seconds after preparation

(λ_{max}) are seen at 320 nm (3.88 eV) and 615 nm (2.02 eV) for the undoped sample, assigned respectively to a π–π^* transition and to an excitonic transition located in the nitrogen[23]. As this polymer solution is doped by the addition of TFA, the excitonic transition associated with the polymer conductivity is shifted to a lower energy (855 nm (1.45 eV)). Further addition of acid caused no further decrease in the transition energy. Similar spectra are observed if the TFA-doped POMA powder is dissolved in DMF. In this case, however, the doping level appears to be higher, as indicated by the lower energy obtained (900–955 nm (1.37–1.29 eV)). Since doped POMA powder was easier to dissolve than its undoped counterpart, and yielded greater polymer doping levels, this was the doping method selected to prepare the POMA stock solutions.

The viscosimetry measurements showed no increase in the viscosity upon doping the polymer in DMF solution (using method (ii), for doping levels of 3.1, 6.25, 12.5, 25, 50 and 100%). This apparently indicates that polymer doping is associated only with the generation of metallic states and not with secondary doping. This latter type of doping was observed recently[24] for parent polyaniline where the chain conformation changing from coil-like to rod-like led to large increases in the viscosity number of the solution.

Under the conditions investigated, it was not possible to prepare blends of the parent polyaniline with PVDF, since the conducting polymer precipitated (forming a two-phase system) upon mixing the two stock solutions prepared with the same co-solvent (NMP). The miscibility of PVDF and the polyaniline derivatives, on the other hand, may be explained by the favourable dipolar interaction between the groups containing the fluorine and oxygen atoms, from the PVDF and alkoxy substituted polyanilines, respectively. One possibility for improving the miscibility of PVDF and PANI was to add poly(vinyl chloride)[11] to this blend, which apparently avoided segregation. These blends, however, possessed low mechanical strength and low conductivity.

Properties of the polyblends

It can be seen in *Figure 2* that the conductivity of PVDF/POAA–TFA blends increased significantly with the content of the latter component. The onset of the conductivity (from 10^{-13} to 10^{-7} S cm^{-1}, respectively, for pure PVDF[13] and for PVDF/POAA–TFA (95/5) blends occurs for lower contents of the conducting material than in the case of conventional metallic fillers ($\sim$16%)[25]. This low percolation threshold had been previously observed for other blends of polyaniline[8–10], and has been attributed to the formation of an unusual interpenetrating network[6]. Interestingly, the conducting polymer remained doped upon mixing with PVDF, even for the blends containing low doping content levels, as no changes were observed in the u.v.-vis. spectra. The conductivity of blends doped in the form of films by method (iii) (6×10^{-4} S cm^{-1} for PVDF/POMA (75/25)) was slightly lower than those (see *Figure 2*) doped by method (i) (1.2×10^{-3} S cm^{-1}). Differing from our results, the first studies[12] on blends of PVDF/POMA indicated a higher percolation threshold (20% POMA) and a lower conductivity (10^{-10} S cm^{-1}). These discrepancies might be due to the use of a less efficient polymer synthesis procedure and/or a lack of optimization of the film preparation conditions. In the work described in ref. 12 POMA was polymerized in a low-acid-concentration solution (0.25 M trifluoromethanesulfonic acid); no additional doping was performed and the polymer was treated at high temperatures (100°C) for a long period of time when dedoping may have occurred.

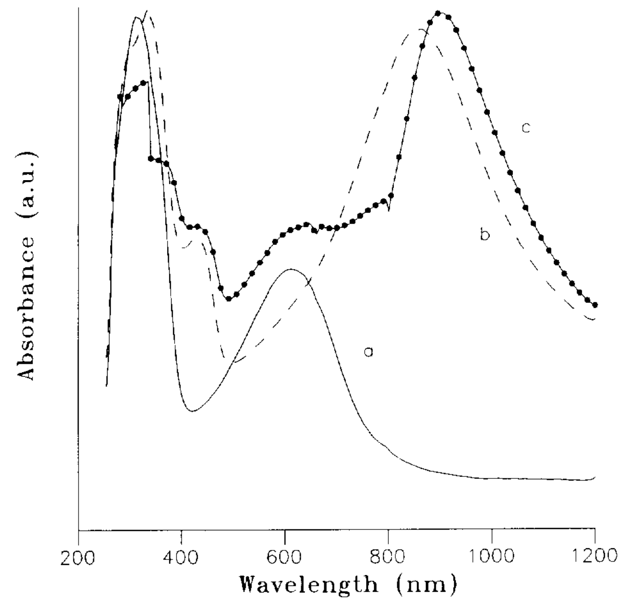

Figure 1 The u.v.-vis. spectra of poly(*o*-methoxyaniline) in DMF solution after different doping treatments: (a) undoped; (b) polymer powder doped with TFA before dissolution; (c) polymer doped after dissolution, by the addition of TFA to the DMF solution

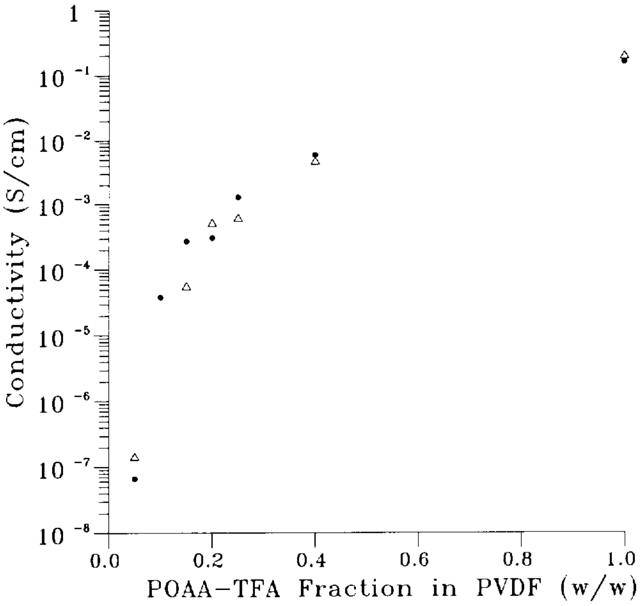

Figure 2 Electrical conductivity *versus* weight fraction of poly(*o*-alkoxyaniline)s doped with TFA (POAA–TFA) in films (cast from DMF) of polyblends with PVDF: (●) poly(*o*-methoxyaniline); (△) poly(*o*-ethoxyaniline)

The electrochemical behaviour of these blends in 1.0 M TFA, investigated by cyclic voltammetry, is shown in *Figure 3*. The first cycle of the cyclic voltammogram presents two redox couples at 0.10 (SCE) and 0.59 V, which are in close agreement with those of pure POMA (0.09 and 0.56 V)[16]. Further cycling of the blends caused

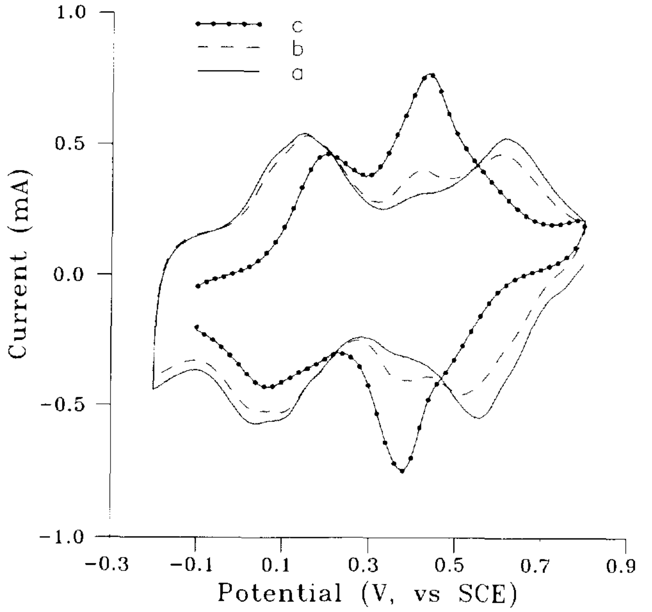

Figure 3 Cyclic voltammograms of the electrochemical response of PVDF/POMA-TFA (60/40) blends: (a) first cycle; (b) fifth cycle; (c) twentieth cycle. Conditions employed: scan rate = 50 mV s^{-1}; 1.0 M TFA

the appearance of an intermediate couple at 0.39 V (0.41 V for pure POMA) and the vanishing of the couple at the highest potential, after the voltammogram had reached a steady-state condition (after ~20 cycles), shown by curve (c) in *Figure 3*. Electroactive blends were obtained even with contents as low as 5% of the conducting POMA component. Moreover, undoped blends also presented electrochemical activity after being placed for just a few seconds in the acid electrolyte media, indicating that a continuous conducting pathway was formed (within the insulating matrix) which is capable of transporting ions. The formation of such a conducting pathway is consistent with the percolation threshold seen in the conductivity data.

Remarkably, an electrochromic effect, with colour changes from light green (at −0.1 V) to dark blue (at 0.8 V), could be seen visually, as a function of the applied potential during the cyclic voltammetry experiments. This arises from an interconversion between the oxidation states of polyanilines, from the leucoemeraldine form (completely reduced) to the pernigraniline (completely oxidized) form[26], caused by reduction–oxidation and protonation–deprotonation reactions. It is surprising that the electrochemical activity of conducting polyblends has not been explored before. Because the blends are highly processible, their electroactive properties may be potentially useful for technological applications such as electrical displays[3].

The X-ray diffraction data presented in *Figure 4* show a dependence of the PVDF crystalline phase on the content of the conducting host in the blend. Under the conditions used (DMF, 70°C) PVDF crystallizes predominantly in the β-phase, but as POMA is added to give ratios varying from 99/1 to 80/20 a considerable amount of the α-phase is formed. This is indicated by the appearance of characteristic peaks for the α-phase[27] at $2\theta = 26.9$ and 18.5°. A diffractogram containing these peaks was observed only when pure PVDF was allowed to crystallize at temperatures above 110°C. For POMA contents greater than 20% the diffractogram indicates the predominance of the β-phase of PVDF and the appearance of a peak due to POMA at $2\theta = 7.7°$. Apparently, small amounts of POMA contribute to the nucleation and crystallization of the α-phase, but this effect vanishes for POMA contents greater than 20%.

Films of these blends were very flexible and had mechanical strengths which were similar to pure PVDF. For polyaniline derivatives, this is particularly important, since they usually present a lower mechanical strength than the parent polyaniline. The use of a polymer, instead of a metallic filler, solves the problem of rendering a conventional polymer conducting. This problem had been addressed before only by the production of composites, which, however, were very brittle. Since these blends possess high tenacity, they could be uniaxially stretched by zone drawing at ratios of up to 5 times their initial length. Films as large as 3 cm wide by 15 cm long, with increased tensile strength, were obtained. Remarkably, after this stretching procedure, blends of, e.g. PVDF/POMA (80/20) (which contains predominantly the α-phase) could be completely converted to the β-phase PVDF, as indicated by the X-ray diffractogram (see *Figure 4*). These results are relevant in so far as PVDF in the β-phase possesses piezoelectric activity.

PVDF is widely used as a dielectric material due to its high dielectric constant. Blends of PVDF have been recently shown to be suitable for capacitor applications[12],

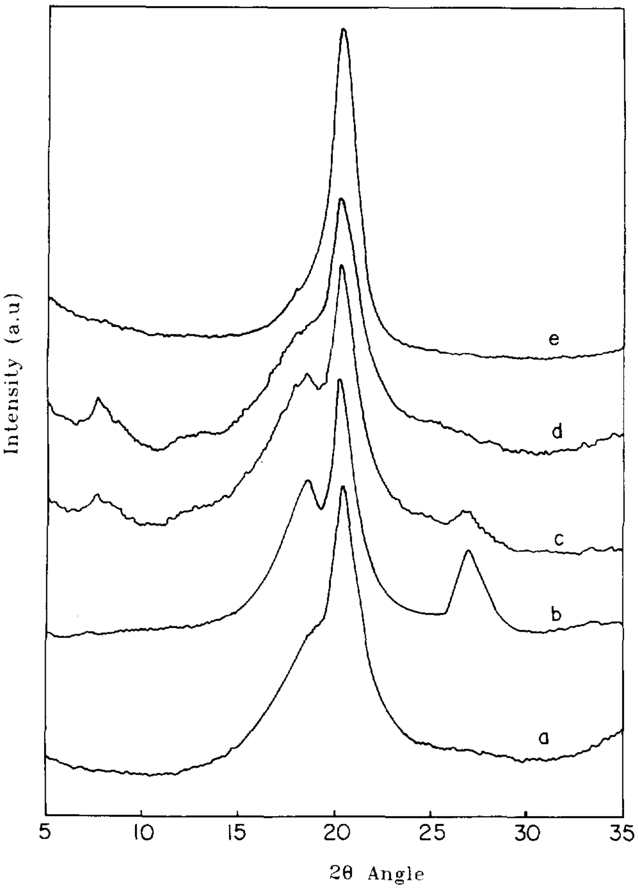

Figure 4 X-ray diffraction patterns of polyblends of PVDF/POMA-TFA with the following ratios: (a) 100/0; (b) 99/1; (c) 80/20; (d) 75/25; (e) 80/20 stretched to give a l/l_0 ratio of 4

because of their large permittivity. Indeed, we have observed that for POMA contents lower than 10% the dielectric constant of these blends can be increased by the presence of the conducting polymer (dielectric constant of 24.8 for the blend containing 5% of POMA). This high bulk capacitance might be due to phase boundary effects (interfacial polarization) promoted by charge buildup at the insulating/conducting polymer interfaces. Differing from the physical dispersion of a conducting ceramic phase in PVDF, these polyblends have the advantage of keeping the flexibility inherent in the PVDF. A more detailed electrical characterization of these blends is currently under way.

CONCLUSION

The conditions for the preparation and doping of blends of poly(alkoxyaniline)s and poly(vinylidene fluoride) have been investigated. In contrast to the parent polyaniline, these derivatives are soluble in several organic solvents, both when undoped or doped with common acids. Doped films of these blends could be obtained by using three different doping procedures: (i) doping the polymer before preparing the solution, (ii) doping the blend dissolved in solution, and (iii) doping the blend in the form of films. Flexible, stretchable and conducting polyblends, which exhibit low percolation thresholds, and conductivities as high as that of the parent conducting polymer, were prepared by casting. These PVDF/POAA blends displayed electrochromism with colour changes similar to that of the polyalkoxyaniline, indicating that a continuous conducting pathway, which is capable of exchanging charge, is formed within the insulating matrix. Blends could also be made to exhibit the β-phase of PVDF by selecting appropriate preparation conditions or by film zone drawing.

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