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Thermal, mechanical and electrochemical behaviour of poly(vinyl chloride)/polypyrrole blends (PVC/PPy)

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The conductivity, thermal, mechanical and electrochemical properties of poly(vinyl chloride)/polypyrrole blends are described in this paper. These blends were prepared by oxidative chemical polymerization of pyrrole, in the vapour phase, in PVC films impregnated with $FeCl_3$. They were characterized by attenuated total reflectance *FT*i.r. spectra, differential scanning calorimetry and dynamic-mechanical analysis. Infrared reflectance spectra suggested that the polymerization occurs preferentially on the matrix surface producing sandwich-type structures. The mechanical, thermal and conducting behaviour showed a dependence on (1) initial concentration of $FeCl_3$ in the matrix and (2) exposition time to pyrrole vapour. By cyclic voltammetry we observe that blends synthesized by oxidative chemical polymerization show electrochemical properties similar to blends prepared by electrochemical methods. Their conductivity varies from 10^{-4} to 10^{-1} S cm^{-1}. Dynamic-mechanical analysis results suggest a certain degree of miscibility among the polymeric components of the blend. Copyright © 1996 Elsevier Science Ltd.

(Keywords: conductive blends; polypyrrole; PVC)

INTRODUCTION

Polypyrrole (PPy) presents electrical conductivity (up to 100 S cm^{-1}, depending on the synthesis method) associated with electrochromic properties, opening perspectives for several potential technological applications[1]. This polymer is synthesized by chemical or electrochemical methods. Depending on the method used, hard and brittle or soft and flexible films are obtained[2]. However, even, flexible films cannot be processed with the technology currently used in the plastics industry. Therefore, one of the possible ways to adjust the mechanical properties of conductive polymers to the processing technology consists of combining PPy with insulating polymers to obtain block and graft copolymers, blends or composites. The most usual method to obtain blends with conductive polymers consists of their incorporation in an insulating matrix by electropolymerization or oxidative polymerization (chemical synthesis) of the adsorbed monomer[2-5]. Blends may show properties inherent to their individual constituents, such as the mechanical properties of the insulating matrix and the conductivity of the conducting polymer, although, with some loss in relation to the pure components. The incorporation of PPy rigid chains in an insulating matrix significantly changes their mechanical properties (increase in the elastic modulus and in the stress at break)[6]; it also reduces the conductivity values in relation to pure PPy[7].

Blends of PVC and PPy were previously obtained by the electrochemical method, using pure PVC or its plasticized form with poly(chloroprene)[3]. It was observed that by increasing the polymerization time it is possible to obtain blends with high PPy concentrations and high conductivity on both faces of the film. The mechanical properties are similar to those of PVC.

High conducting (15 S cm^{-1}) poly(vinyl alcohol)/PPy (PVA/PPy) blends have been prepared by the chemical method using PVA films impregnated with $FeCl_3$. Spectroscopic data showed that Fe^{3+} in PVA is reduced to Fe^{2+} and that PPy is uniformly distributed in the PVA matrix[8]. The same method was used by other authors to prepare transparent films of PVC/PPy blends[9]. These authors suggest a mechanism with formation of the counter-ion $FeCl_4^-$ (compensating the positive charge of PPy) and HCl. Transparent and conductive (20 S cm^{-1}) films of PVC/PPy were also prepared by initial impregnation of PVC with the pyrrole monomer and subsequent immersion in a binary solvent–oxidative solution system[10].

Transmission electron micrograph analysis of the films showed formation of a PPy layer within 0.1 μm of thickness of the film surface. A layered structure film was also obtained by interphase oxidative polymerization of pyrrole on a PVC membrane separating an organic pyrrole solution and a $FeCl_3$ aqueous solution[11]. The effects of the hydration degree of the oxidant $FeCl_3$ incorporated in PVC and of the solvent, used to incorporate the iron salt in the insulating matrix, on the

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microwave absorbing properties of the PVC/PPy blend were also reported[12].

In this work we report on the study of the conductivity, thermal, mechanical and electrochemical properties of the PVC/PPy blends prepared by the oxidative polymerization process.

EXPERIMENTAL

PVC films, 0.1 mm thick, impregnated with $FeCl_3$ at 0, 1, 5, 10, 20 and 35% concentrations (mol/mol) were obtained by casting a tetrahydrofuran (THF) solution containing PVC (Solvay do Brazil, M_n 70 000 g mol^{-1}) and $FeCl_3$ (Merck, 99%) in different relative concentrations. THF was evaporated at 45°C and the films were dried in vacuum at ambient temperature. The PVC/PPy blends were obtained by exposure of the PVC/$FeCl_3$ films to pyrrole vapour for 2 h or 6 h at ambient temperature and pressure in a closed vessel.

Attenuated total reflectance (ATR) *FT*i.r. spectra for 0.1-mm thick PVC films impregnated with 20% of $FeCl_3$ and PVC/PPy blend, obtained after 6-h exposure to pyrrole vapour, were measured in a Perkin–Elmer 1600 *FT*i.r. at 1 cm^{-1} resolution. Thermogravimetric analyses were carried out in a DuPont 951 thermal analyser under argon flow. Samples of ca. 30 mg were heated from 25 to 950°C at 10°C min^{-1}. Stress–strain tests were performed in an EMIC-MEM 500 equipment, interfaced to a PC/XT computer, according to ASTM D 882-64T, at 25°C, using a 500 N detector cell and a cross-head speed of 5 mm min^{-1}.

Differential scanning calorimetry (d.s.c.) measurements were done in a DuPont 910 Thermal Analyzer, using the following temperature programme: (1) temperature jump to 140°C; (2) cooling slope to −140°C at 20°C min^{-1}; (3) isotherm at −140°C for 5 min; (4) heating to 140°C at 20°C min^{-1}. The curves shown in this article correspond to the fourth step.

Dynamic-mechanical analyses (d.m.a.) were done in a DuPont 983 DMA analyser. The samples were heated from −100°C to 200°C at 2°C min^{-1}, with a constant frequency of 1 Hz and oscillation amplitude of 0.1 mm.

The conductivities were measured using four-point probe equipment from Alessi Industries coupled to a Keithley model 530 instrument (current source model 225CS and digital voltmeter model 163DV). Film samples were measured on both faces.

Cyclic voltammetry measurements were carried out at ambient temperature in a single-compartment cell, under argon flux, containing as electrolyte a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Aldrich, 99%) in dry acetonitrile. Working electrodes were prepared by depositing PVC/$FeCl_3$ 20% films ($\cong$10 μm thick) on platinum foils, followed by exposure to pyrrole vapour for 64 h. The counter electrode was also platinum and an Ag/AgCl double junction Ingold EA 441/5 electrode was used as reference. Samples were preconditioned for six cycles from −0.90 to 0.90 V at 0.10 V s^{-1}, before registration of the curve. A FAC-200A Potentiostat/Galvanostat interfaced to a PC/XT type computer (ramp generator and recorder) was used.

RESULTS AND DISCUSSION

Attenuated total reflectance *FT*i.r. spectroscopy was used to characterize the heterocyclic monomer polymerization in the PVC insulating matrix. *Figure 1* shows the *FT*i.r./ATR spectra of PVC films impregnated with 20% of $FeCl_3$, and of the PVC/PPy blend obtained by exposure of this matrix to pyrrole vapour for 6 h. The spectrum of the PVC/PPy blend is clearly different from that of the original matrix. The spectrum of the blend shows

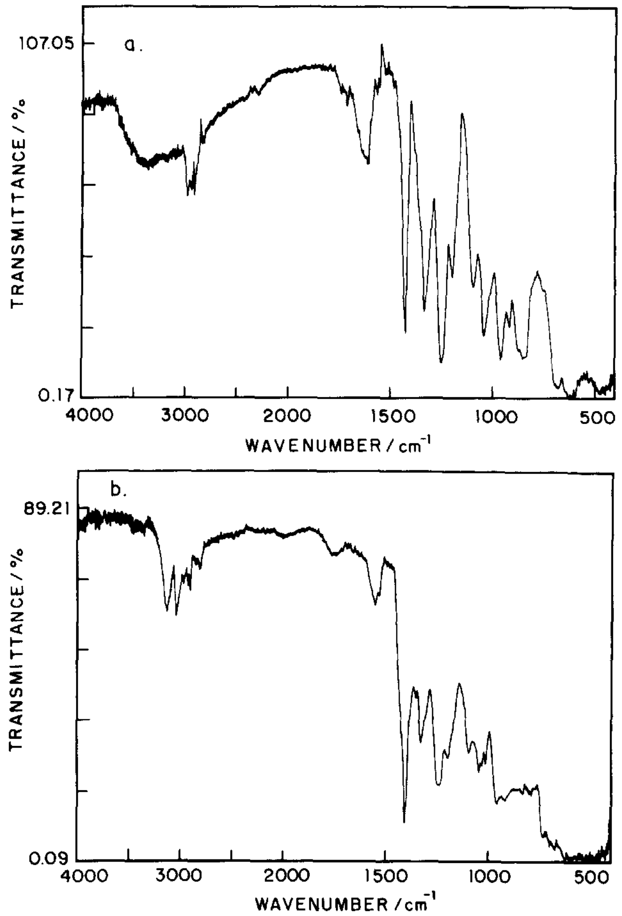

Figure 1 *FT*i.r./ATR spectra of (a) PVC/$FeCl_3$ 20% film and (b) PVC/PPy blend obtained after 6 h exposure to pyrrole vapours

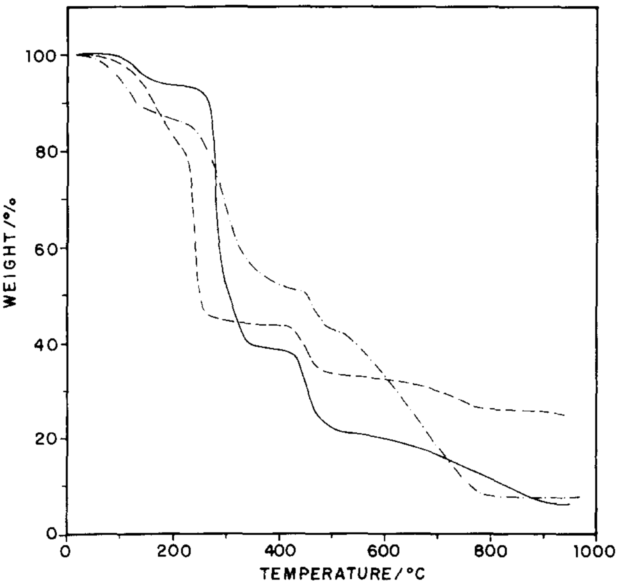

Figure 2 Thermogravimetric curves (10°C min^{-1}): (—) pure PVC, (- - -) PVC/$FeCl_3$ 20% and (- · -) PVC/PPy blends

absorptions that confirm the incorporation of the conductive polymer: 1552 cm^{-1} (aromatic C = C stretching), 1030 cm^{-1} (N–H deformation), 900 cm^{-1} and 700 cm^{-1} (out-of-plane C–H vibrations)[3,13]. The ATR technique provides information about the sample at the surface level, thus the identification of PPy characteristic bands shows that the polymerization occurs preferentially on the surface of the matrix, producing a concentration gradient of conductive polymer and 'sandwich' type structures. Similar results were reported in the electropolymerization of pyrrole in PVC[14] and in the oxidative chemical polymerization of pyrrole in poly(vinyl alcohol)[15].

In *Figure 2* we compare the thermal stability, under argon atmosphere, of: pure PVC, PVC impregnated with 20% of $FeCl_3$ (PVC/$FeCl_3$ 20%) and the PVC/PPy blend obtained by exposure of the PVC/$FeCl_3$ 20% matrix to pyrrole vapours for 6 h. All samples began to lose mass at temperatures below 100°C; however, a greater mass loss is observed for the PVC/PPy blend. For films obtained by casting from THF solutions with or without $FeCl_3$ incorporation, we proved, in a previous work, that this initial loss results from residual solvent evaporation and $FeCl_3$ dehydration[16]. Volatilization of monomers and oligomers adsorbed in the matrix can be also responsible for this initial mass loss. The PVC/$FeCl_3$ 20% sample shows a second mass loss starting at a temperature lower than for pure PVC. The processes occurring from 280°C to 450°C for pure PVC and for the blend can be related to PVC dehydrochlorination. A third mass loss at ca. 450°C occurs for all three samples and can be assigned to cross-linking of the conjugated double bonds generated in the dehydrochlorination process. For the blend, a fourth mass loss is observed at ca. 550°C and is assigned to conductive polymer degradation. These results show that there is no interference of the PVC degradation process on the thermal behaviour of the conductive polymer, because the t.g.a. curves of the blend resemble a superposition of the pure PVC curve with the pure PPy curve.

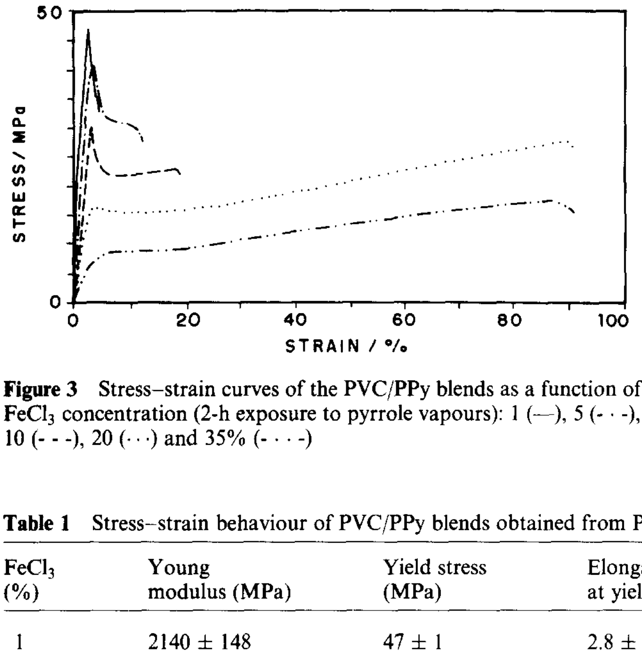

Figure 3 Stress–strain curves of the PVC/PPy blends as a function of $FeCl_3$ concentration (2-h exposure to pyrrole vapours): 1 (—), 5 (- · · -), 10 (- - -), 20 (· · ·) and 35% (- · · · -)

Figure 3 shows the stress–strain behaviour of the PVC/PPy blends, obtained by exposure to pyrrole vapour for 2 h, as a function of the initial $FeCl_3$ concentration in the matrix. Pure PPy films behave like hard and brittle material, with high elastic modulus (ca. 10^9 Pa), high stress at break (ca. 64 MPa), and short elongation at break (lower than 5%), breaking without drawing[17]. Conversely the mechanical properties of PVC change from hard and brittle to soft and tough, depending on the degree of $FeCl_3$ incorporation[16]. The exposition of the PVC/$FeCl_3$ matrices to pyrrole vapours during 2 h results in blends with mechanical behaviour that is more like the precursor than pure PPY (*Table 1* and *Figure 3*). The plasticization effect observed previously due to impregnation of PVC with $FeCl_3$ is maintained after pyrrole polymerization[16]. Increasing the exposure time to 6 h causes a plasticization effect that produces blends with final mechanical properties different from those of the original matrix (*Table 2* and *Figure 4*). This occurs because, with the increase in the exposure time, there is an increase in the amount of PPy incorporated, resulting in harder and more brittle blends. The fact that, even after 6 h exposure, the PVC/PPy blends show the plasticization effect, shows that PPy

Table 1 Stress–strain behaviour of PVC/PPy blends obtained from PVC/$FeCl_3$ matrices and exposed to pyrrole for 2 h

$FeCl_3$ (%)	Young modulus (MPa)	Yield stress (MPa)	Elongation at yield (%)	Stress at break (MPa)	Elongation at break (%)	Work to break ($J/10^{-3}$)
1	2140 ± 148	47 ± 1	2.8 ± 0.2	35 ± 2	4.0 ± 0.2	61 ± 8
5	1708 ± 89	40 ± 2	3.1 ± 0.3	30 ± 2	11 ± 9	124 ± 106
10	1515 ± 242	30 ± 3	2.8 ± 0.4	22 ± 2	19 ± 12	199 ± 65
20	884 ± 107	17 ± 3	3.8 ± 0.6	28 ± 7	90 ± 30	498 ± 216
35	288 ± 62	7 ± 2	5.4 ± 0.6	17 ± 5	89 ± 31	331 ± 244

Table 2 Stress–strain behaviour of PVC/PPy blends obtained from PVC/$FeCl_3$ matrices and exposed to pyrrole for 6 h

$FeCl_3$ (%)	Young modulus (MPa)	Yield stress (MPa)	Elongation at yield (%)	Stress at break (MPa)	Elongation at break (%)	Work to break ($J/10^{-3}$)
1	2102 ± 188	46 ± 4	2.8 ± 0.5	38 ± 5	6 ± 1	68 ± 15
5	1699 ± 117	40 ± 1	3.4 ± 0.4	25 ± 9	23 ± 16	189 ± 107
10	1725 ± 129	38 ± 3	3.0 ± 0.3	27 ± 2	14 ± 9	134 ± 92
20	1418 ± 86	28 ± 2	3.6 ± 0.1	29 ± 9	68 ± 34	612 ± 489
35	320 ± 48	8 ± 1	5.1 ± 0.8	10 ± 1	69 ± 17	260 ± 74

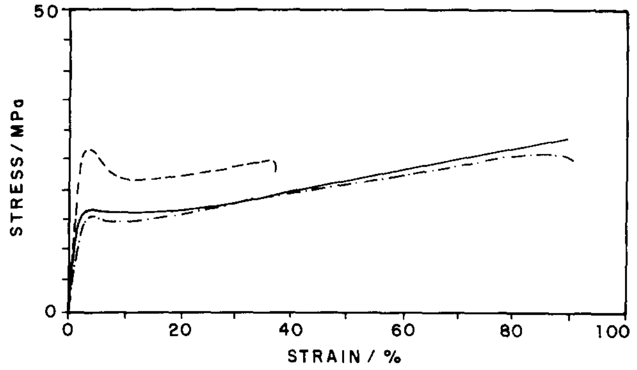

Figure 4 Stress–strain curves for films of PVC/FeCl$_3$ 20% (- · -) and PVC/PPy blends after 2 h (—) and 6 h (- - -) exposure to pyrrole vapour

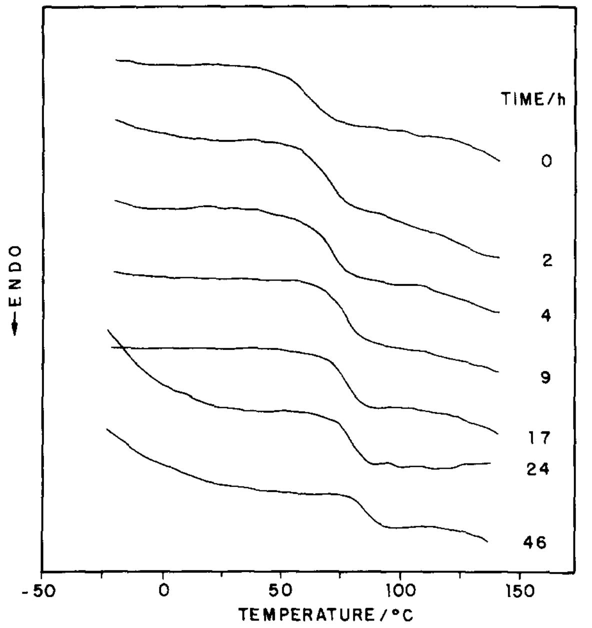

Figure 5 D.s.c. curves (20°C min^{-1}) as a function of the exposure time to pyrrole vapours, for PVC/PPy blends obtained from PVC/FeCl$_3$ 20% matrices

polymerization begins from the surface to the bulk of the PVC film, giving rise to a concentration gradient of the conductive polymer.

From d.s.c. measurements we observed that the PVC/PPy blends show glass transition temperatures dependent on the exposure time to pyrrole vapours and oxidant agent concentration in the original PVC matrix (*Figure 5* and *Figure 6*, respectively). The variation of the mass of polypyrrole, incorporated in the PVC/FeCl$_3$ 20% matrix, and the variation of the glass-transition temperature of the resulting blend as a function of exposure time to pyrrole vapours are plotted in *Figure 7*. We note that T_g of the PVC/PPy blends shifts to higher temperatures with the increase in the exposure time. However, within experimental error, there is a stabilization in the rate of PPy incorporation after 4 h, suggesting that the increase in T_g is not associated with the increment in PPy quantity in the blend. The increase in the exposure time can cause an increment in the blend stiffness, owing to growing and cross-linking of conducive polymer chains, resulting in an increment in the T_g[18]. Comparing the T_g variation as a function of FeCl$_3$ concentration in the blends (from the thermograms of

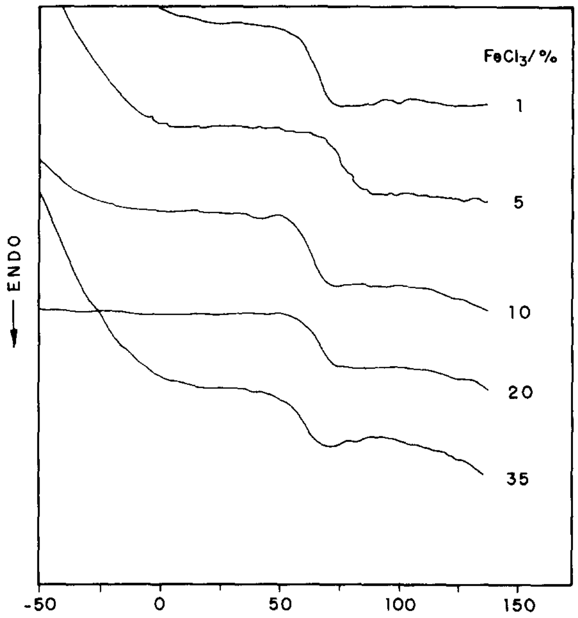

Figure 6 D.s.c. curves (20°C min^{-1}), as a function of initial FeCl$_3$ concentration in PVC/FeCl$_3$ films, for PVC/PPy blends obtained after 6 h exposure to pyrrole vapour

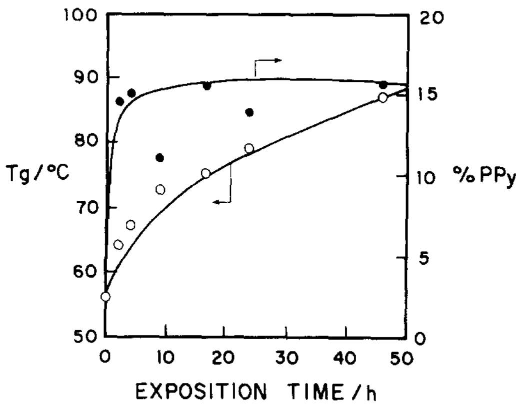

Figure 7 Per cent mass of PPy incorporated and T_g of PVC/PPy blends as a function of exposure time of the PVC/FeCl$_3$ 20% matrices to pyrrole vapour

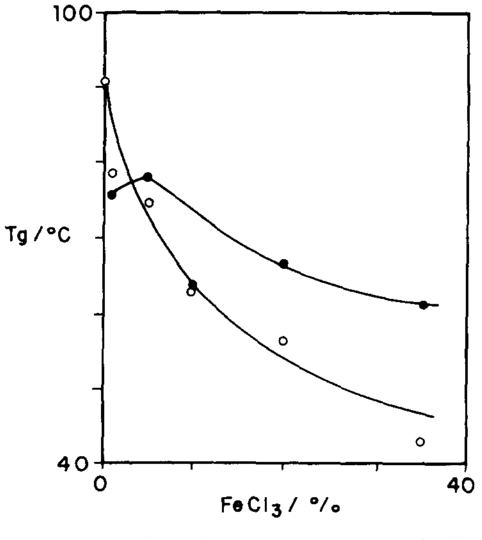

Figure 8 Dependence of Tg with FeCl$_3$ concentration in films of: (○) PVC/FeCl$_3$ and (●) PVC/PPy

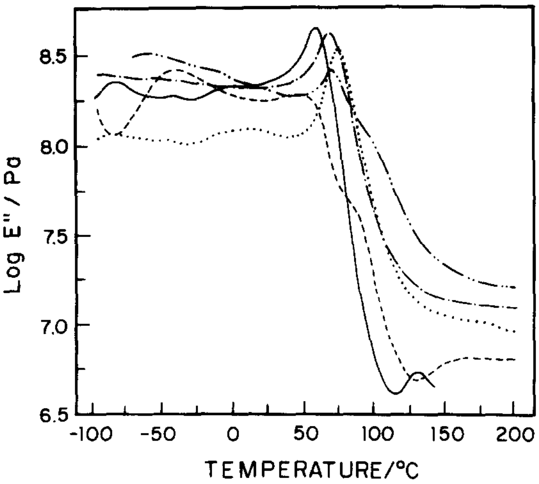

Figure 9 Log E'' as a function of temperature for PPy/PVC blends with different exposure times to pyrrole vapour: — 0, - - - 4, ····· 8, -·-·-· 24, and -··-··- 72 h

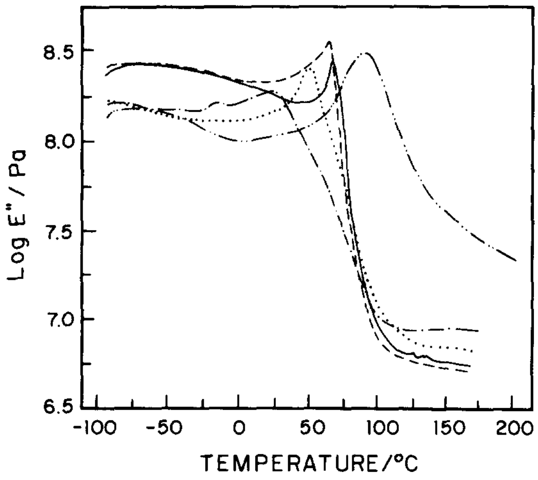

Figure 10 Log E'' as a function of temperature for PPy/PVC blends for different FeCl$_3$ concentrations in the PVC/FeCl$_3$ films (exposure time = 6 h): — 1.0, - - - 5.0, ····· 10.0, -·-·-· 20.0, and -··-··- 35.0% FeCl$_3$

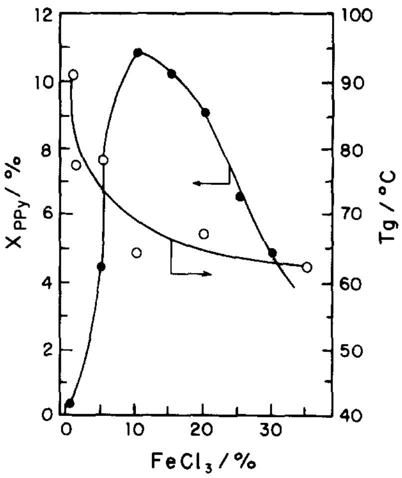

Figure 11 PPy concentration in the blends and T_g as a function of FeCl$_3$ concentration in the PVC/FeCl$_3$ films. Exposure time was 6 h

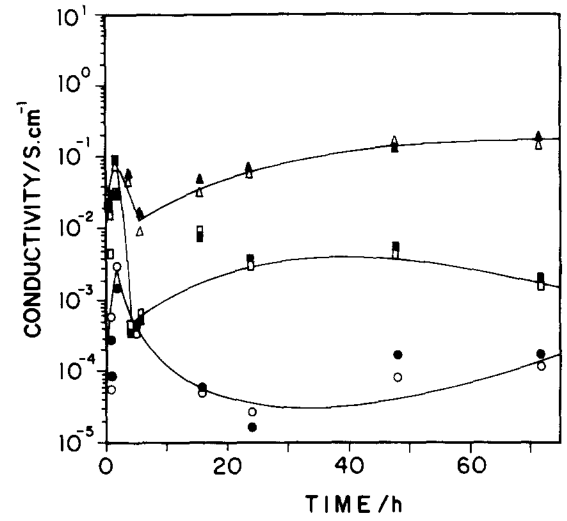

Figure 12 Variation of the conductivity of PVC/PPy blends, obtained from PVC/FeCl$_3$ 20%, as a function of time of exposure to pyrrole vapours and temperature. Open and closed symbols represent the conductivity measured at both faces of the films. ▲△ 25°C; ■□ 50°C; and ●○ 70°C

Figure 6) and in PVC films (from ref. 16), we observe a similar trend for T_g variation of the blends, but shifted to higher temperatures (*Figure 8*). This is expected because of the incorporation of the more rigid chains of the conductive polymer.

Dynamic mechanical analyses were made on PVC/PPy blends obtained from PVC/FeCl$_3$ matrices in various concentrations of oxidant agent and different times of exposure. *Figure 9* shows $\log E'' \times T$ for the blends of PVC/FeCl$_3$ 20% matrices as a function of exposure time to pyrrole vapours. We observe an increase in the number of relaxation processes for blends obtained by exposure to pyrrole vapour up to 4 h. These new relaxation processes are assigned to pyrrole oligomers in the PVC matrix because they disappear or shift to higher temperature with increase of exposure time, although the PPy concentration changes little at exposure times longer than 4 h (*Figure 7*). *Figure 10* shows $\log E'' \times T$ for blends obtained from exposure of PVC/FeCl$_3$ films, in various concentrations of the oxidant agent, to pyrrole vapours during 6 h. The E'' peak is broad for blends prepared from PVC/FeCl$_3$ 10% and PVC/FeCl$_3$ 20% showing phase separation. For other compositions there are no differences between PVC/FeCl$_3$ and its blends. The blend composition is responsible for this behaviour because it strongly changes with FeCl$_3$ content in PVC (*Figure 11*): PPy concentration is maximal for a FeCl$_3$ concentration of 10%. The d.s.c. thermograms[18] show one defined T_g, independent of exposure time or blend composition, suggesting miscibility, while d.m.a. furnishes more details about phase behaviour of PVC/PPy blends.

The conductivity of the blends prepared from PVC/FeCl$_3$ 20% was studied as a function of exposure time to pyrrole and temperature, *Figure 12*. The highest conductivity is observed after 6 h reaction at 25°C (0.1 S cm^{-1}), and remains constant after 70 h. The exposure to pyrrole vapours for periods of 7 days increases the amount of polypyrrole incorporated in the matrix by a factor of 100%, but the conductivity remains constant. Increase in temperature to 75°C accelerates polypyrrole incorporation, but results in a drop of three orders of magnitude in the conductivity. This is probably caused by oxidation of the polypyrrole chain concomitant with the polymerization, thus reducing the conductivity.

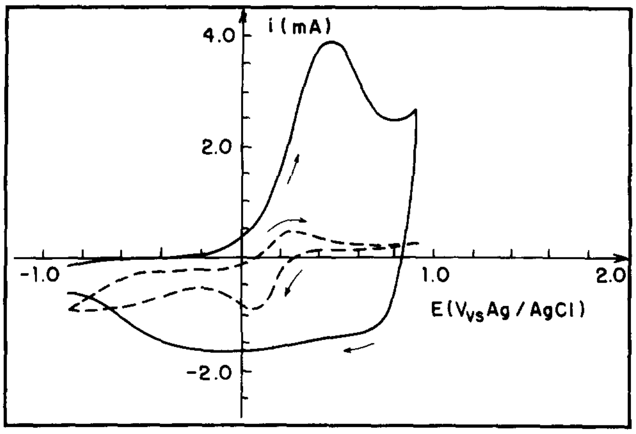

Figure 13 Cyclic voltammetry curves (10 mV s^{-1}) for the PVC/PPy blend (—) and for the PVC/$FeCl_3$ 20% film (- - -)

Polypyrrole can be electrochemically cycled between the conductor (oxidized) and nonconductor (neutral) states. The redox reaction includes oxidation of the conjugated π system of the conductive polymer chain followed by ion insertion and deinsertion (doping/undoping), necessary to keep electroneutrality[19,20]. The doping/undoping ratio is dependent on the diffusion rate of the ion and, consequently, on the polymer morphology[21]. Conditioning of PPy electrodes is normally required to reach an equilibrium state of electroactivity. This is obtained by repeating the potential scans until the voltammograms become reproducible. In *Figure 13* we show the cyclic voltammograms corresponding to the sixth cycle of potential scan of the PVC/$FeCl_3$ 20% film and the PVC/PPy blend obtained by exposure of this film to pyrrole vapours for 64 h. A much longer exposure time is required because the PVC/$FeCl_3$ 20% is deposited on a platinum foil and only one face is exposed. For the PVC/PPy blend we note a well-defined anodic oxidation peak at 0.40 V and a broad cathodic reduction wave. These redox processes are assigned to PPy, because the processes related to $FeCl_3$ occur at different potentials with significantly smaller current peaks. For the blend we also observe a high capacitive current in the anodic potential region, probably due to an increment in the effective electrode area when in the oxidized state (conductor). The cathodic wave, representing the undoping process, is not well-defined because of the film thickness ($\cong$ 10 μm) which precludes diffusion of the dopant ions. This effect is not observed with the anodic wave because the oxidation process is faster than the reduction one[22]. The high anodic and cathodic peak currents and the stability to the redox cycles show that PPy segregation through the PVC matrix does not significantly change the electrochemical properties of the conductive polymer.

CONCLUSIONS

The chemical oxidative polymerization method is efficient for the preparation of blends composed of PVC and PPy, with conductivities ranging from 10^{-4} to 10^{-1} S cm^{-1}. The incorporation of PPy in the PVC matrix was confirmed by *FT*i.r./ATR and the possibility for formation of 'sandwich' type structures was noted. The blending of PPy in PVC does not change the thermal behaviour of the conductive polymer. We noted that there was phase separation resulting from the low solubility of the polymeric components. The stress–strain behaviour and the T_g of the blends are dependent on the initial $FeCl_3$ concentration and the exposure time to pyrrole vapours. These blends, obtained by a chemical method, showed similar electroactivity to those obtained electrochemically, however, the electroactivity is clearly influenced by the presence of the insulating matrix.

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