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Electrically Conducting Polyaniline–Poly(acrylic acid) Blends

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Abstract: We report an electrically conducting polyaniline–poly(acrylic acid) blend coatings prepared by mixing the emeraldine base (EB) form of polyaniline (PANI) and poly(acrylic acid) (PAA) aqueous solution. The samples show a moderate electrical conductivity σ. If they are immersed in an HCl aqueous solution, the conductivity of the samples is increased by two or three orders of magnitude and their thermal stability is also improved. Optical transmittance spectra show a complete protonation of PANI–PAA blends after immersion in HCl aqueous solution. Fourier transform infrared spectroscopy studies indicate that the better thermal stability of σ could come from the more stable protonated imine nitrogen ions. A low percolation threshold phenomenon is observed in PANI–PAA blends, from a strong interaction between the carboxylic acid groups of PAA and the nitrogen atoms of PANI. © 1998 SCI.

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Key words: polyaniline; poly(acrylic acid); polymer blends; electrical conductivity; FTIR spectroscopy; percolation; conducting polymer composite

INTRODUCTION

Polyaniline represents a class of macromolecules whose electrical conductivity can be varied from insulating to metallic by a redox process. The general formula of these polymers is $[(\text{—B—NH—B—NH—})_y(\text{—B—N=Q=N—})_{1-y}]_x$, in which B and Q denote C_6H_4 rings in the benzenoid and quinoid forms, respectively.[1–4] The conducting state of polyaniline (PANI) can be achieved, for example, by the protonation of the imine nitrogens (=N—) in its 50% oxidized emeraldine state ($y = 0{\cdot}5$; also called emeraldine base, EB) in an aqueous acid such as HCl. The protonated polymer (emeraldine salt, ES) is a polysemiquinone radical cation consisting of two separated polarons. The spreading out of the polaron wavefunction onto the neighbouring rings results in the formation of a delocalized half-filled broad polaron energy band.[3]

One problem associated with the HCl doped polyaniline is its ease of dedoping by ageing, or by contact with water, and consequently the loss of its electrical conductivity. It is believed that the dopant species are so small that they can be evaporated, or sublimed out of the polymer.[5,6] To overcome this drawback, several polymeric acids have been used as dopants, such as poly(acrylic acid),[4–6] poly(styrenesulphonic acid),[4,5] among others, as given in ref. 6. Although both X-ray photoelectron spectroscopic studies[4] and dynamic mechanical results[6] show an inefficient protonation of polyaniline films by polymeric acids, the stability of the polymeric acid doped polyaniline is improved in a higher pH solution[6] and its glass transition temperature is higher than that of the PANI film.[6]

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From the point of view of its role as a binding material, poly(acrylic acid) (PAA) has been successfully used to develop metal oxide–PAA composites for dental applications[7,8] and in electrically conductive CuS–PAA coatings.[9] In the latter case, a p-type semiconductor CuS powder was dispersed in PAA aqueous solutions and then coated on a glass substrate. The sheet resistance of the coatings as a function of CuS concentration showed a percolation phenomenon, giving a sharp insulator–conductor transition for CuS contents of less than 40 wt%. In this respect, the behaviour of PAA as an insulating polymeric matrix is like that of polyvinyl chloride, or polyester resins, in carbon black–polymer composites.[10] In the case of electrically conducting polymer–polymer blends or composites, however, the percolative aspect is somewhat peculiar. For example, in conducting gels of ultrahigh-molecular-weight polyethylene (insulator) and the soluble conjugated polymer poly(3-octylthiophene) (conductor), there is evidence for the presence of connected conducting paths with no indication of a well defined percolation threshold.[11] The absence of a sharp insulator–conductor transition has also been reported in polyaniline composite systems such as PANI in a copolymer latex[12] and in poly(methylmethacrylate).[13]

In the present work we report that the lack of a sharp insulator–conductor transition observed in PANI–polymer composites is also true with PANI–PAA blends. We also report on the thermal stability of electrical conductivity up to 170°C of some of these blends, and relate this stability to the imine nitrogen protonation of the material as evidenced from the Fourier transform infrared (FTIR) spectra. The optical transmittance spectra of the samples show the complete protonation of PANI–PAA blends with additional HCl doping.

EXPERIMENTAL

Preparation of the polymer blend coatings

The emeraldine salt (ES, the electrically conducting state of polyaniline) is barely soluble in common organic solvents, whereas emeraldine base (EB, deprotonated ES and the insulator state of polyaniline) can easily be dissolved, for example, in *N*-methylpyrrolidione (NMP). Therefore, it is usual first to prepare thin films of EB and then to convert them into conducting films by soaking them in an aqueous acid. In the present work, the EB powder was precipitated from a chemical bath prepared as follows: to an aqueous solution of 60 ml of 0·1 M $(NH_4)_2S_2O_8$ and 30 ml of 1 M HCl, kept under stirring at room temperature (26°C), 1·2 ml of aniline monomer was added dropwise. After about 5 h stirring, 20 ml of concentrated NH_4OH was added to the solution, which changed its colour from dark green to dark blue. The resulting mixture was left for about 15 h to precipitate and then filtered. The precipitate was rinsed with an abundant amount of deionized water until the filtrate was colourless, and then dried at 50°C for about 18 h. Finally it was dissolved in NMP, giving a dark blue solution of EB.

Both aniline monomer and NMP were supplied by J. T. Baker Co. The poly(acrylic acid) (supplied by Aldrich) used in this work was in the form of an aqueous solution containing 25 wt% of the polymer. The average molecular weight of PAA was listed as 90 000. Mixtures of the EB and PAA solutions were prepared and cast on clean glass slides to give thick coatings (10–15 μm), or the glass slides were dipped in the mixtures to obtain thin films (less than 1 μm). The coatings were dried at 50–60°C in an air oven, and the colour in transmission of dried EB–PAA blend coatings was green or dark green, or even black with increasing thickness.

A smooth and reflective coating of EB–PAA blend can be obtained for a relatively low molar proportion of EB to PAA, namely from unity to around 0·24 (based on the approximate repeat unit $-C_6H_4NH-$ in EB and the repeat unit $-CH_2CHCOOH-$ in PAA), which corresponds to a weight percentage range of EB in EB–PAA blends from 55% to around 23%. As the EB : PAA molar proportion decreased, the coatings became opaque (from 0·24 to 0·15) and even sticky (lower than 0·15). With a molar proportion below 0·04 the coating was badly formed and was considered useless for electrical measurements.

The electrical conductivity of the PANI(EB)–PAA samples could be improved by soaking them in a 1 M HCl aqueous solution for a few seconds. We will refer to them in the following discussion as PANI–PAA samples with HCl doping.

Characterization

Pairs of silver print electrodes (5 mm length at 5 mm separation) were painted on the EB–PAA coatings to enable sheet resistance ($R_\square$) measurement. The electrical conductivity ($\sigma = 1/R_\square d$) of the samples was calculated knowing the coating thickness (d). Optical transmittance spectra of the coatings were recorded on a Shimadzu UV3101PC spectrophotometer. Fourier transform infrared (FTIR) spectroscopy studies were made in the transmittance mode with a Nicolet-5SX spectrophotometer. The same spectra, as a function of temperature between 20 and 300°C, were recorded on a laboratory-designed resistance heating system coupled with the same spectrophotometer. The electrical current versus temperature curves of typical samples were obtained by heating them in a laboratory designed oven connected with a computerized data processing

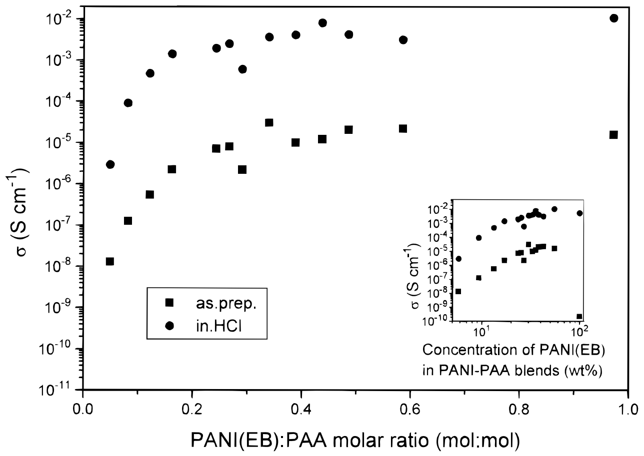

Fig. 1. Electrical conductivity (σ) of PANI–PAA blend coatings as a function of PANI(EB) : PAA molar ratio. The inset shows the same data on a log–log scale, but as a function of PANI(EB) weight percent in the coatings.

system.[14] This system consisted of an HP 4140B pA meter/DC voltage source, an HP3421A data acquisition/control unit, an HP6024A DC power supply and an HP216/9000 personal computer.

RESULTS AND DISCUSSION

Electrical properties

Composite materials have long been known to have electrical properties very different from those of their constituents. Classical percolation theory[15,16] predicts that for a composite comprising two materials with electrical conductivities σ_1 and σ_2 (with $\sigma_1 \gg \sigma_2$), the effective conductivity σ_e exhibits a power law (in the limit in which σ_2 approaches zero) of $\sigma_e = \sigma_1\ (p - p_c)^t$,

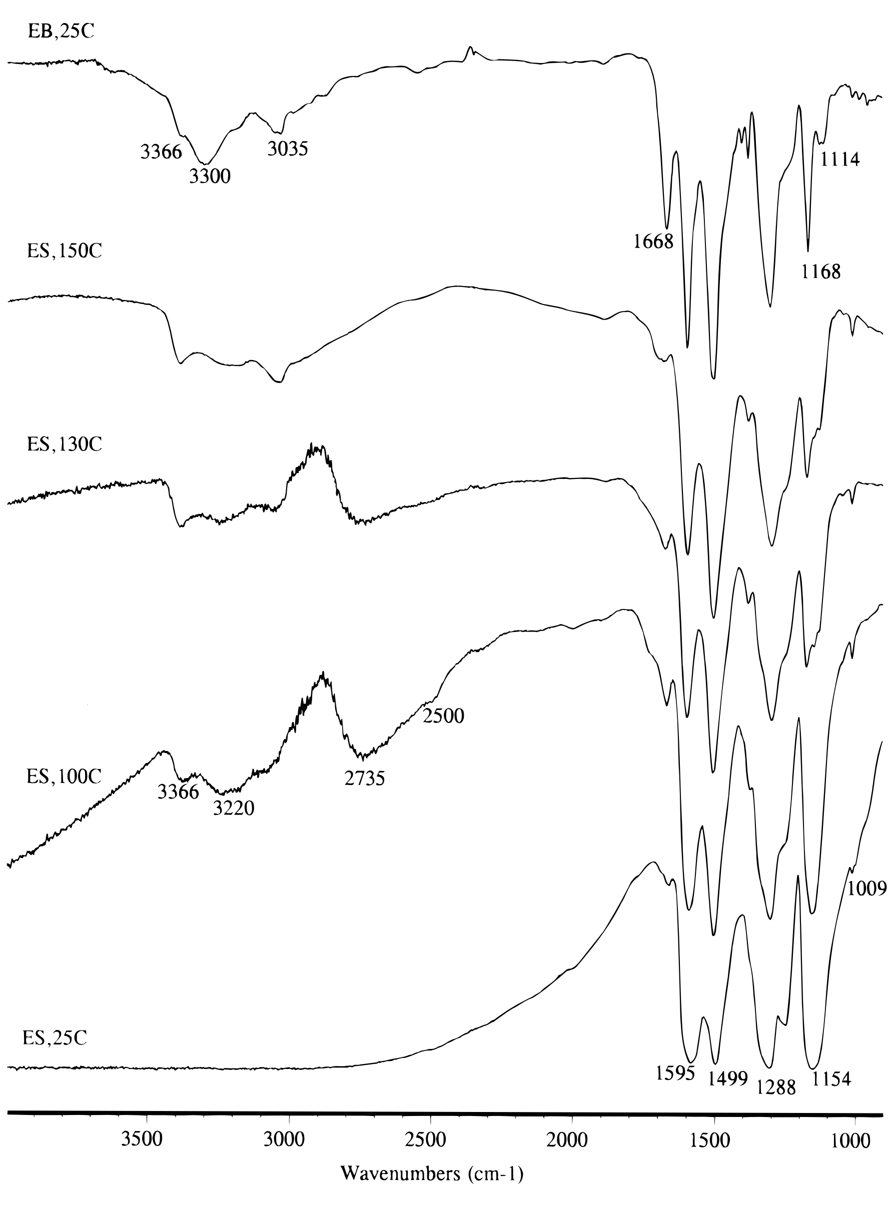

Fig. 2. FTIR spectra of PANI(EB) free standing film at 25°C and PANI(ES) free standing films at 25, 100, 130 and 150°C.

where p is the volume, or mass (weight) fraction of material 1, p_c is the percolation threshold for material 1, and the exponent t is believed to depend on the dimensions of the composite, and is somehow universal for the same materials. We note that the electrical properties of many composites, for example CuS–PAA coatings,[9] show such a percolation phenomenon. However, in the case of PANI–PAA blends, the variation of electrical conductivity with composition given in Fig. 1 does not indicate a well-defined percolation threshold. Such a result is in agreement with that observed in a poly(3-octylthiophene)–ultrahigh-molecular weight polyethylene (P3OT–UHMW PE) gel system.[11] We see that for PANI–PAA coatings the conductivity follows a simple power law $\sigma_e = cp^\alpha$ over the range of EB : PAA molar proportion from 0·24 to 0·05 (concentration of EB from 23 to around 5·5 wt%; see inset of Fig. 1). The value of α is close to 2·6, which is the same as that reported in ref. 11 for the P3OT–UHMW PE gel systems.

The very small content of P3OT for the onset of conductivity in the P3OT–UHMW PE gels is explained on the basis that the P3OT conjugated chains are adsorbed onto the PE network because of a strong interaction between the two polymers.[11] The same kind of interaction was also suggested for PANI–PAA blends by XRD patterns: a distortion of the PAA matrix occurred in the presence of PANI.[6] From previous work on metal oxide–PAA composites,[7,8] we suggest that possible interactions between PANI and PAA could be taking place between the carboxylic groups (—COOH) of PAA and imine nitrogens and/or amine nitrogens of PANI. FTIR studies on EB, ES and PANI–PAA blends given below clarify the details of these interactions.

FTIR studies of PANI–PAA blends

Figure 2 shows the FTIR transmittance spectra of EB and ES free standing films at room temperature. The protonation of EB is identified by the presence of a strong and broadened absorption band at about 1154 cm^{-1}. This has been ascribed to a high degree of electron delocalization in polyaniline.[6,17,18] The narrowness and a slight shift to higher frequency of this band suggests an insulating emeraldine base,[17] as can be seen in the spectrum of the EB sample.

For the ES sample the transmittance in the 4000 to 2000 cm^{-1} range is very low, implying a high absorption by free water on the sample surface. The films were heated in a laboratory designed resistance heating oven, which was integrated into the FTIR spectrophotometer, permitting *in situ* measurement of FTIR spectra at different temperatures for the same sample. In Fig. 2 the FTIR spectra of ES free standing films at temperatures higher than room temperature are also shown. The broad absorption bands around 2735 cm^{-1} are clearly observed in the ES sample at heating temperatures higher than 80°C, and these disappear above 130°C. Following the suggestion in ref. 19, this absorption

TABLE 1. FTIR bands (cm^{-1}) for EB and ES forms of PANI

EB, 25°C	ES			Assignment
	25°C	100°C	130°C	
3366 m, sh		3366 m	3366 w	ν(N—H), 2° amine[20,21]
3300 m, b				ν(N—H), 2° amine[20,21]
		3220 m, b	3220 w, b	H-bonded ν(N—H)[18,20]
3035 w			3035 w, b	ν(C—H) aromatic[21]
		2735 m, b	2735 w, b	ν(N$^+$—H) and overtones in Fermi resonance[20]
				ν(NH$_2^+$) in saturated amine[19]
		2500 w, sh		ν(NH$^+$) in unsaturated amine[19]
1668 m	1668 w	1668 w	1668 w	ν(C=N) iminoquinone[19,21]
1595 s	1595 vs, b	1595 s	1595 s	ν(C=C) of the quinoid rings[6]
1499 vs	1499 vs, b	1499 vs	1499 vs	ν(C=C) of the benzenoid rings[6]
1403 vw				
1372 vw		1372 vw	1372 w	ν(C—N) in QB$_t$Q[18]
1288 s	1288 vs, b	1288 vs	1288 s	ν(C—N) in QB$_c$Q, QBB, BBQ[18]
1246 w	1246 s	1246 m, sh	1246 m, sh	ν(C—N) in BBB[18]
1168 s, n	1154 vs, b	1154 vs, b	1170 m	electronic like absorption of N=Q=N[6,17]
			1146 w	
1126 vw			1130 w	
1114 vw				ν(C—H) aromatic[21]
1009 vw	1009 vw	1009 vw	1009 vw	ν(C—H) aromatic[21]

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; n, narrow; sh, shoulder; ν, stretching; Q, quinoid ring; B, benzenoid ring; B$_t$, *trans* benzenoid unit; B$_c$, *cis* benzenoid unit.

band could be assigned to the antisymmetrical and symmetrical stretching vibrations of protonated amine nitrogen ions NH_2^+, $\nu_{as}(NH_2^+)$ and $\nu_s(NH_2^+)$. The bending deformation band of NH_2^+ should be around $1600\,cm^{-1}$, which could be superimposed on the strong stretching band of C=C in quinoid rings. The weak shoulder close to $2500\,cm^{-1}$ could be ascribed to the stretching mode of protonated imine nitrogen ions NH^+. In the HCl protonated PANI samples, therefore, the protonation could be taking place preferentially on amine nitrogen atoms. Table 1 lists the assignment of the observed absorption bands.

The FTIR transmittance spectra of the PANI–PAA samples (Fig. 3, for the sample with an EB : PAA molar proportion of 0·34, or an EB concentration in EB–PAA blend of 30 wt%) exhibit two important features. Firstly, compared with the HCl protonated PANI samples (ES), the stretching band of protonated nitrogen of the PANI–PAA sample is shifted to a lower frequency around $2500\,cm^{-1}$, suggesting a preferential protonation of imine nitrogens in the case of PAA protonated polyaniline films. The same conclusion was drawn from XPS studies on the PANI–PAA systems.[4] Secondly, a new band at $1628\,cm^{-1}$ is present from room temperature to about 115°C, which is shifted to $1665\,cm^{-1}$ at higher temperatures. This band could be the convolution of a bending vibration [δ(OH)] of the water molecule and the asymmetrical stretching of the carboxylate group (—COO) resulting from the acid–base reaction[20] between PAA and PANI. The symmetrical stretching of the carboxylate group may be represented by the $1407\,cm^{-1}$ band, superimposing on the ν(C—O) and

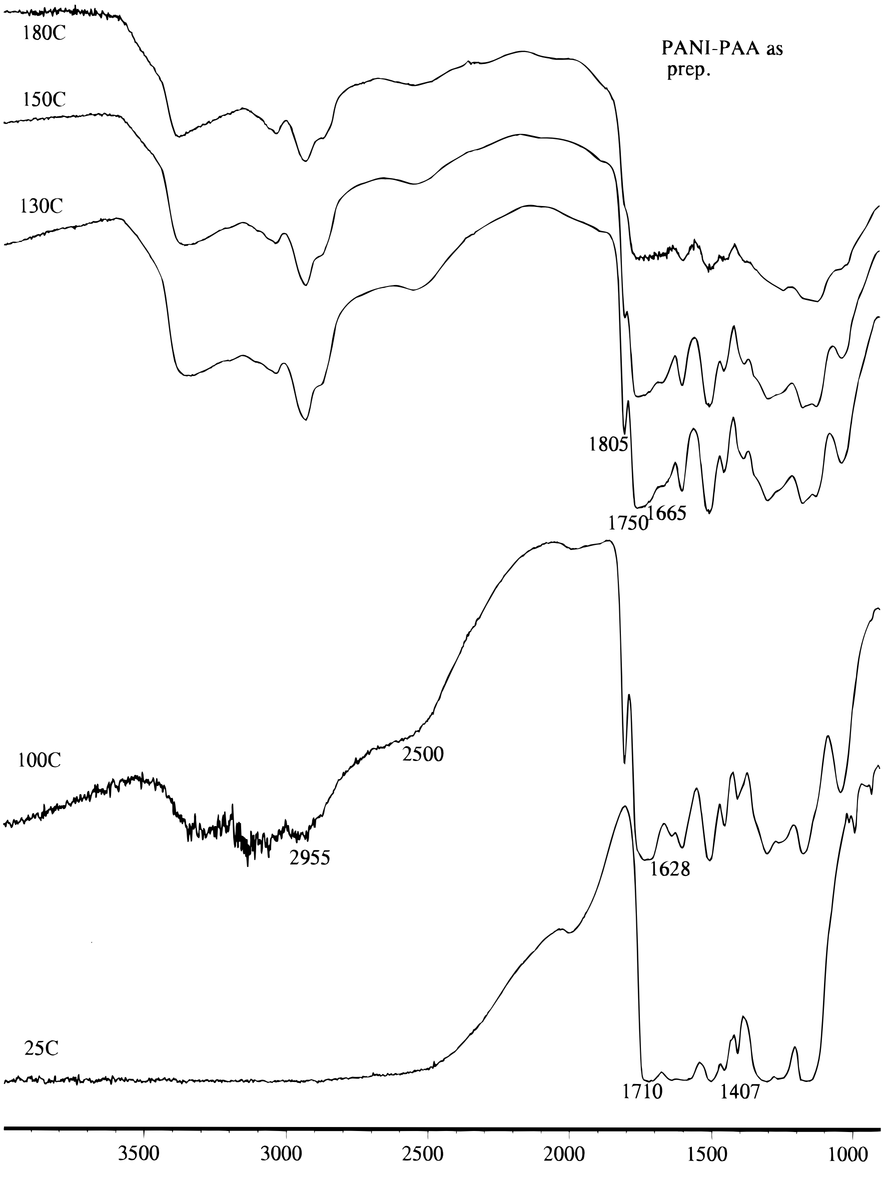

Fig. 3. FTIR spectra of PANI–PAA blend free standing films with EB : PAA molar ratio equal to 0·34 at 25, 100, 130, 150 and 180°C.

TABLE 2. FTIR bands (cm^{-1}) for as prepared PANI–PAA samples with an EB : PAA molar ratio equal to 0·34

25°C	100°C	130°C	Assignment
	3300 s, b	3300 m, b	ν(N—H), 2° amine[20,21]
	2955 s, b	2931 m	(1) ν(O—H) of COOH[19] (2) $\nu(CH_2)$ of PAA
	2500 m, b	2500 w	$\nu(N^+—H)$ and overtones in Fermi resonance[20] $\nu(NH_2^+)$ in saturated amine[19]
	1805 s	1805 m	
		1750 s, b	ν(C=O) of PAA[19,20]
1710 vs, b	1710 vs, b		ν(C=O) of PAA[19,20]
		1665 mb	ν(C=N) iminoquinone[19,21]
1628 s	1628 m		(1) ν_{as} (CO_2) of carboxylates[20]; (2) δ(OH) of water[19]
1595 s	1595 s	1595 s	ν(C=C) of the quinoid rings[6]
1499 s	1499 s	1499 s	ν(C=C) of the benzenoid rings[6]
1450 m	1450 m	1450 m	$\delta(CH_2)$[19]
1407 w	1407 w		(1)δ(OH) + ν(CO) of —COOH[19]; (2) ν_s (CO_2) of carboxylates[20]
		1387 w	ν(C—N) in QB_tQ[18]
1288 s	1288 s	1288 s	ν(C—N) in QB_cQ, QBB, BBQ[18]
1246 m	1246 m		(1) ν(C—N) in BBB[18]; (2) δ(OH) + υ(CO)[19]
1154 s	1154 s	1170 s	(1) electronic like absorption of N=Q=N[6,17]; (2) δ(OH) of —COOH[22]
		1130 m	
	1027 m	1027 m	
1009 w	1009 vw	1009 vw	ν(C—H) aromatic[20]

Abbrevations: s, strong; m, medium; w, weak; v, very; b, broad; n, narrow; sh, shoulder; ν, stretching; ν_{as}, antisymmetrical stretching; ν_s, symmetrical stretching; δ, deformation; Q, quinoid ring; B, benzenoid ring; B_t, *trans* benzenoid unit; B_c, *cis* benzenoid unit.

δ(OH) bands of carboxylic acid group of PAA. The assignments of the bands are listed in Table 2.

When the temperature is around 100°C, two more absorption bands are present in the PANI–PAA samples, at 1805 cm^{-1} and 1027 cm^{-1}. Their intensity starts to decrease from 150°C and they vanish at 180°C. We do not have a specific assignment for these bands, but their parallel evolution as a function of temperature indicates a close relationship between them. Further studies are needed to establish the origin of these absorption bands.

Effect of HCl doping of the PANI–PAA blends

It is interesting to observe that non-protonated carboxylic acid groups of PAA in the PANI–PAA blends are present from room temperature up to 150°C, as shown by the presence of carbonyl stretch bands (1710–1740 cm^{-1}), and the interaction bands between C—O stretch and C—O—H in-plane bending (1407 cm^{-1} and 1246 cm^{-1}). This is another indication that PAA is not an efficient doping agent for polyaniline, in agreement with what was suggested elsewhere.[4,6]

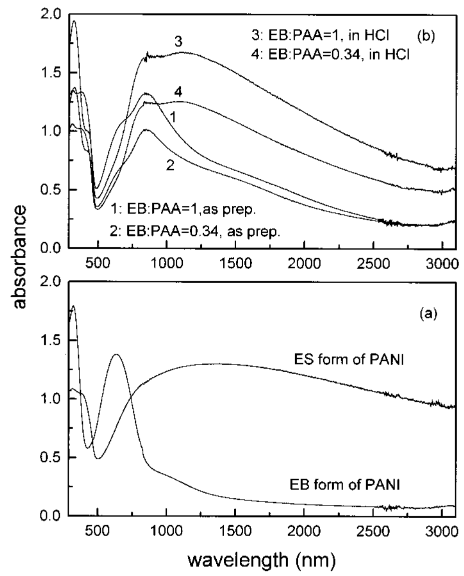

Fig. 4. Optical properties of PANI–PAA blend coatings: (a) EB and ES forms of PANI; (b) curves 1 and 3: as prepared and with additional HCl doping, respectively, of PANI–PAA blend with EB : PAA molar ratio equal to 1; curves 2 and 4: as prepared and with additional HCl doping, respectively, of PANI–PAA blend with EB : PAA molar ratio equal to 0·34.

However, we have seen in Fig. 1 that if we soak the blends in an HCl aqueous solution, their conductivity is raised by about two or three orders of magnitude, independent of the PANI concentration in the blend. From the optical properties of the samples (Fig. 4), it is observed that the intensities of two absorption peaks due to the π–π^* transition of the benzenoid rings (324 nm) and the exciton absorption of the quinoid rings (639 nm)[6] decrease considerably after immersion in HCl solution, indicating the oxidation of the EB phase present in the as-prepared PANI–PAA blends.

To examine the effect of this second doping on the molecular structure of the blend, the FTIR spectra of the same PANI–PAA molar proportion 0·34 (or 30 wt% of EB) samples with additional HCl doping were taken and are shown in Fig. 5. In this case, the maximum of the protonated nitrogen absorption band appears around 2540 cm^{-1}, as was observed with PANI–PAA (Fig. 3). However, compared with the PANI–PAA samples, the 1628 cm^{-1} band is absent and the 1407 cm^{-1} band is a little weaker. From these changes of the FTIR spectra it is possible, in the doping with HCl of the PANI–PAA samples, to draw the following conclusions: (a) The protonation of the nitrogen still occurs preferentially on the imine nitrogen, but with a higher efficiency than in the PANI–PAA samples, as indicated by the increase of the intensity of the corresponding band. In other words, the PAA seems to favour the imine nitrogen protonation. (b) The 1 M HCl aqueous solution used in this work has a pH near zero, and the PAA water solution shows a pH around 1·5. Because of the stronger acidic character of HCl, the doping of PANI–PAA samples with HCl results not only in the protonation of imine, or amine nitrogen

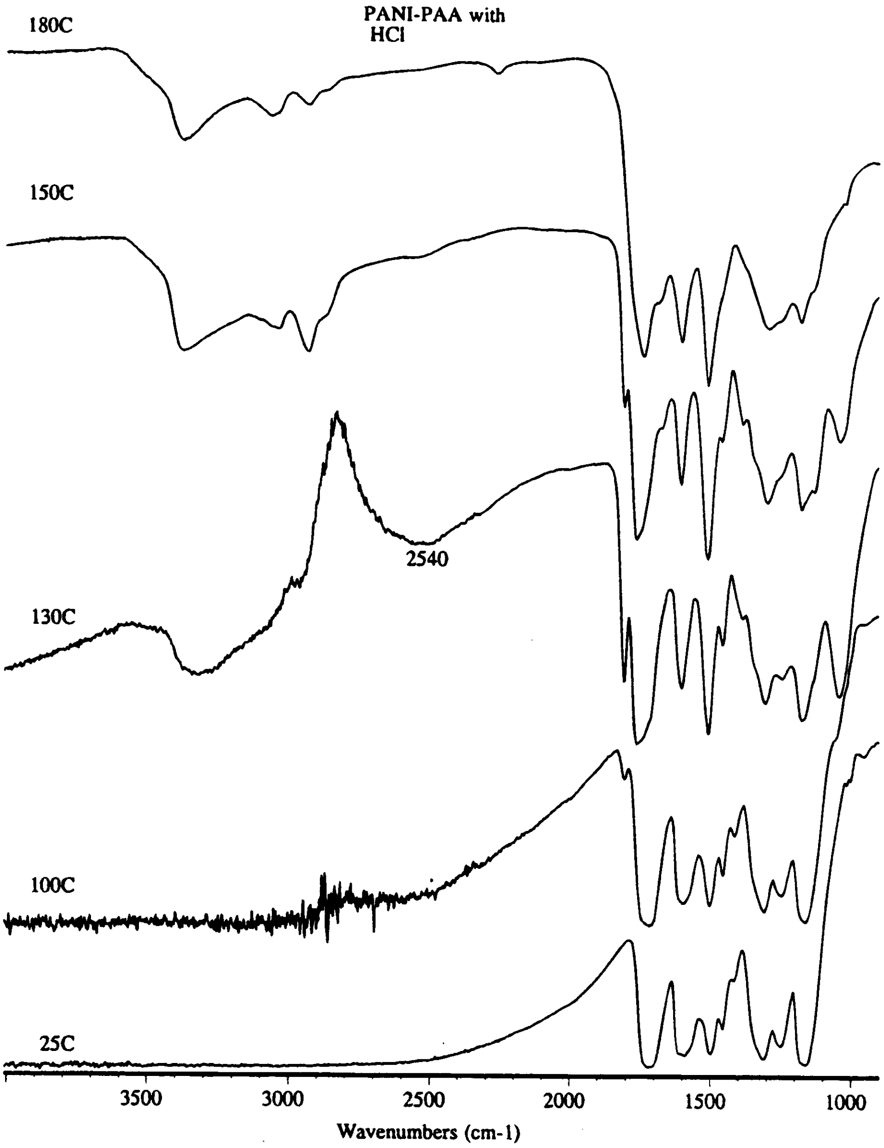

Fig. 5. FTIR spectra of HCl doped PANI–PAA blend free standing films with EB : PAA molar ratio equal to 0·34 at 25, 100, 130, 150 and 180°C.

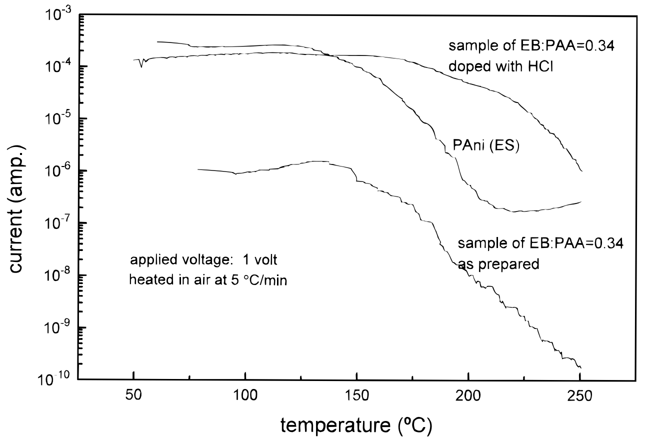

Fig. 6. Electrical currents as a function of temperature of PANI(ES) coating and as prepared, and HCl doped PANI–PAA blend coatings with EB : PAA molar ratio equal to 0·34.

atoms in PANI (indicated by the increase in electrical current shown in Fig. 6), but also in the re-protonation of the carboxylate groups (—COO) of PAA, which act as a conjugated base for the HCl. Therefore, the carboxylate anions behave as receptors of the volatile protons of hydrochloric acid, giving a better thermal stability of the electrical conductivity of the samples.

Figure 6 shows the electrical current as a function of temperature for the various materials prepared in this study. The current recorded in the ES coating starts to drop from about 130°C, because of the evaporation of the HCl molecules (and hence the disappearance of protonated amine nitrogen bands (Fig. 2)). The PANI–PAA samples exhibit a similar thermal stability, probably because of the decomposition of the carboxylate ions (the $1628\,\mathrm{cm}^{-1}$ band, Fig. 3) at about 130°C, liberating protons from the samples. The PANI–PAA samples doped with HCl are, however, stable up to around 170°C, as we suggested above. Finally from the point of view of bond strength, the protonation of the imine nitrogen to give $(=\mathrm{C}-\mathrm{NH}-\mathrm{C})^+$ would be more favoured than that of the amine nitrogen to give $(-\mathrm{C}-\mathrm{NH}_2-\mathrm{C})^+$, and this could also be the reason for the PANI–PAA samples with HCl doping being more stable than the ES samples.

The low percolation effect in PANI-PAA blends

We would like to address the issue of the nature of the intermolecular interaction between the two polymers, which relates to the PANI–PAA blends being low percolative materials. It seems that an interaction occurs between the carboxylic acid groups —COOH of PAA and the imine nitrogen atoms of PANI. In the case of PANI–PAA samples, the interaction is predominantly ionic, between the carboxylate anions and the protonated imine cations. In the PANI–PAA samples with additional HCl doping, the interaction could occur as a hydrogen bond between the hydrogen of the imine nitrogen and the oxygen of the carboxylic groups of PAA. Because the interaction in both cases is at a molecular level, a low concentration of conductive phase can give an electrical path for conduction through the blend. Conversely, in an inorganic–organic composite the conductive phase consists of conglomerated particles of micrometre size. This mixture between two phases is of low efficiency, in the sense that a conductive path must be formed by contact between conductive particles and not molecules. The minimum concentration of the conductive phase in such a composite necessary to form a first conductive path (the percolation threshold) is consequently higher.

CONCLUSIONS

Polyaniline–polyacrylic acid blend coatings were prepared and studied. The electrical conductivities of the coatings as a function of polyaniline concentration exhibit a low percolation threshold, resulting from molecular interactions between the polymers. The FTIR spectra as a function of temperature show a preferential protonation of amine nitrogen atoms in HCl doped PANI films, whereas in PANI–PAA samples the imine nitrogen atoms were predominantly protonated by PAA. The loss of electrical conductivity in both cases, at temperatures higher than 130°C, is probably because of HCl evaporation and/or the decomposition of carboxylates of PAA (the acid–base reaction products between PAA and PANI). With additional HCl doping on PANI–PAA samples, however, the preferential protonation on imine nitrogen atoms gives a higher thermal stability of the electrical conductivity of the coatings, maintaining the same value as that of HCl-doped PANI (ES) films, but at temperatures up to 170°C.

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