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Characterization of PVDF-PPy composite membranes

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The present work is concerned with preparation and characterization of conducting composite membranes and degradation studies in dry atmosphere, water and other environments similar to practical application media. Improvement of the stability, mainly by incorporation of sulfonic stabilizer is another aspect of this work. This work has focused upon chemical oxidation to form the conducting polymers onto host membranes. Development of preferred preparation conditions involves a factorial orthogonal approach, where conductivity and water flux data are pooled from the results of three variables (temperature, concentration and time) at three levels. Morphological changes of membranes surface and cross-section before and after treatment is undertaken using field emission scanning electron microscopy. Chemical structure changes upon degradation in different media is studied by X-ray photoelectron spectroscopy. These studies demonstrate that the incorporation of sulfonate dopants can improve the environmental stability of these membranes by modifying their chemical structure. © 1997 Elsevier Science Ltd.

(Keywords: polypyrrole; PVDF microfilter; X-ray photoelectron spectroscopy)

INTRODUCTION

Membranes are highly energy efficient separators, but still possess inadequate permselectivity, low permeation flux and inadequate membrane durability and fouling characteristics. These limitations are mainly attributed to the inherent structure/property characteristics of the membrane.

Composite membranes modified with intrinsically conducting polymers may provide novel separation capabilities when used with external fields. Unlike conventional charged membranes they may control surface charges through electrical currents. Whilst in principle improved membranes can be made using a conducting polymer modification route from a practical and in particular commercial viewpoint, there are several other issues which need to be considered. These include the selection of hosts with desirable properties. High flux and selectivity generally have the higher priority, but chemical resistance and other factors are also important. Cost, geometry and the capacity for scale-up are other issues. For these reasons we have focused in the present work on chemical routes to polypyrrole (PPy) synthesis rather than the more tedious electrochemical alternative, although the latter can lead to higher conductivity and durability[1]. A further requirement in practice is for the membrane to have predictable properties during its lifetime. The conductivity of conducting polymers has been shown, however, to be sensitive in the presence of oxygen in the water[2]. This is expected to be similarly problematic for composite membranes and related systems such as colloids, as has been shown in several preliminary papers, and as outlined in more detail below.

Composite membranes using non-conducting polymers have been well established with examples being described by Cadotte *et al.*[3]. In these cases the attributes of the skin (high selectivity) are combined with those of the support (high flux), to give a unique combination of properties. However, this class is static by nature, and little scope exists to address reduction in flux (fouling), a major limitation of most membranes.

The formation of conducting polymer/host membrane composites has been previously described by Martin *et al.*[4] and ourselves[5,6], although complete experimental details were not disclosed. This omission is rectified in the present paper.

The ageing behaviour of conducting polymers has been rather thoroughly studied using various techniques. Conductivity decay, changes in morphology and thermal analysis are commonly used[7,8]. To date, the single most useful experimental method has been X-ray photoelectron spectroscopy (X.p.s.), as this technique can provide simultaneous chemical and electronic structural information. It is non-destructive and extremely surface sensitive. An important advantage of X.p.s. is its ability to obtain information on chemical states from variations in binding energies or chemical shifts of the photoelectron lines (core-level spectra). Some basic studies of the surface chemistry of conducting polymers are already well established by different groups[9,11].

However, similar ageing studies for composites using X.p.s. have appeared much less frequently, with the main emphasis being on colloids[12,13]. Exceptions are the Makhlouki *et al.*[14] and Bensiddik *et al.*[15] papers, where X.p.s. has been used for PPy/PVA composites, although in these cases detailed morphology is not disclosed and the composites are modified films rather than porous membranes.

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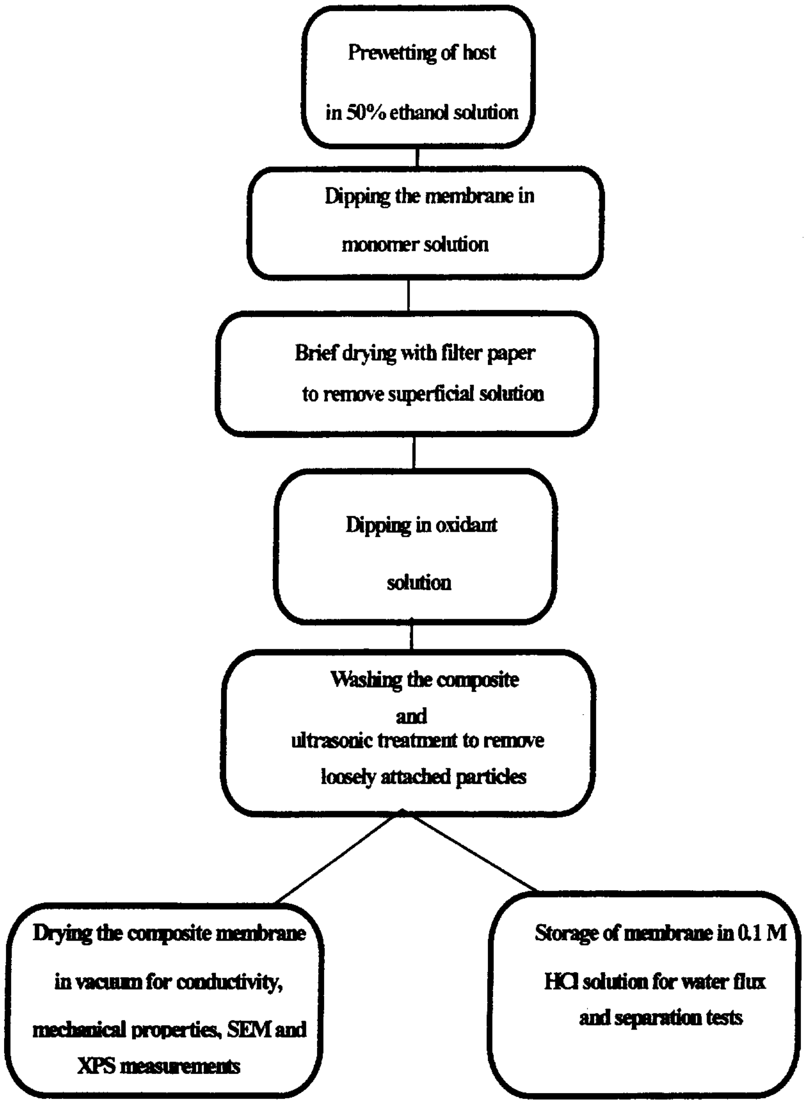


Figure 1 Schematic presentation of preparation of unmodified composite membranes

Aspects of fundamental studies, including changes affecting conductivity such as oxidation[16], loss of conjugation and dopant depletion[17] are now widely known. Similarly changes during doping for both PPy films and powder have been recently reported by Kim *et al.*[10]. Multi-elemental analysis not only provides more information about the structural and chemical defects in conducting polymer, but allows separation of, for example, dopant and polymer backbone changes. For example, by analysing C, O, N and S, changes in oxidation of PPy can in principle be separated from deterioration of sulfur dopant or sulfur-containing stabilizer.

In the present work we report the characteristics of PPy modified microfiltration membranes. Changes during storage of these laminates in different environments and the relation between room-temperature conductivity, stability and chemical structure of these membranes are the main foci.

EXPERIMENTAL

Materials

Pyrrole (Sigma Chemical Co.) was distilled, purged with nitrogen and kept at 0°C until shortly before use. Ferric chloride hexahydrate (BDH, an oxidant for the chemical polymerization of pyrrole) and other chemicals including sulfonated additives (Aldrich) were analytical grade and were used without further purification. 'Milli Q' deionized water was used in the preparation of all aqueous solutions.

Microfiltration hydrophobic PVDF membranes ('GVHP', Millipore), with a stated average pore diameter of 0.22 μm, were used as substrates.

Characterization techniques

X-ray photoelectron spectroscopy. X.p.s. or electron spectrocsopy for chemical analysis (e.s.c.a.) was performed with a Kratos XSAM 800 cpi surface analysis system. The X-ray radiation source was polychromatic Mg–K$_\alpha$. Data acquisition and treatment were carried out with a computer. High resolution scans with a good signal-to-noise ratio were obtained with the magnesium source operating at 12.5 kV and 12 mA. This power rating did not cause any detectable damage to the samples, as in the majority of experiments almost identical spectra for each sample were obtained when the binding energy scans were repeated. The pressure in the chamber was maintained at 10^{-8} mbar or lower. The electron detector pass energy which defines the size of the window in the analyser that photoelectrons may pass through has a significant effect on signal resolution. Higher pass energy gives a more intense signal, but lower resolution. A low pass energy (40 eV) was chosen for peak shape analysis and stoichiometric determinations, while wide scan experiments were performed at a higher pass energy (80 eV) to reduce experiment time. Data were resolved in 'fix analysis transmittance' (FAT) mode. Surface elemental analysis was obtained from peak area ratios after being corrected with sensitivity factors[18].

Doping ratio is defined as the ratio of incorporated counterion to nitrogen. For composites prepared using oxidant as the only doping agent, the doping ratio is equal to Cl^-/N and for samples which were hybridized by doping species, either during polymerization or in post-treatment stages, the sum of sulfur and chlorine was included in the estimation of doping ratio. The analysis depth for these samples is expected to be less than 10 Å. X.p.s. data processing programs have been experimentally derived from sensitivity factors, taking into account the machine-derived factors.

Polymer samples in powder form and the composites in film form were mounted on the standard copper sample studs by means of double-sided adhesive tapes. The samples had a area about 0.5 cm^2 and were aligned at an angle of 90° with respect to energy analyser slits.

Argon ion bombardment is usually used in X.p.s. analysis to clean or etch surfaces; this allows overlayers of contamination or oxidation layers to be removed to allow examination of the underlying material. It is also used for depth profiling, as in the present case. For selected samples, ion-sputter 'depth profiling' was carried out to identify dopant distribution and doping level at different layers of composites. For spectral deconvolution, the full width of half maximum (FWHM) of the Gaussian peak components was kept constant in a particular spectrum.

Conductivity. The electrical conductivity of composite membranes was measured based on ASTM D4496-87. For all samples at least eight measurements at different currents were done, and the resistivity was obtained by regression analysis. Measurements were made on three samples. The environmental stability was determined as conductivity decay with time in various aqueous media of low and high pH and moderate ionic strength. The relative (normalized) conductivity at time $t(\sigma_t/\sigma_0)$ was calculated and reported as a function of exposure time. For each experiment at least three samples with the same initial conductivity were examined. Prior to measurement, samples stored in different environments were rinsed with distilled water and dried with nitrogen gas.

Preparation of composite membranes

Composite membranes of PPy and GVHP were prepared by two-step *in situ* chemical polymerization of pyrrole into host membranes. In general, the following experimental protocol, as summarized in *Figure 1* was followed.

Host membranes were pre-wetted by soaking in aqueous ethanol solution for 10–15 min. After rinsing with water, membranes were immersed in an aqueous pyrrole solution, blot-dried and then immersed in aqueous oxidant solution. The resulting composite membranes were rinsed with copious amounts of water and then immersed in an ultrasonic bath to remove loosely attached superficial particles of PPy.

Chemical polymerization of pyrrole has been studied for several decades. The basis for our work were the reports of Liang *et al.*[19] and Yamaura *et al.*[20], in which a $FeCl_3$/pyrrole molar ratio of 2–2.4/1 was said to be ideal.

Data presented here are for GVHP microfilter/PPy composites. This substrate was chosen mainly due to its chemical resistance, mechanical strength and broad application in separation processes. Development of preferred conditions for coating has involved a factorial orthogonal approach, where conductivity and water flux data is pooled from the results of three variables (temperature, concentration and time) each at three levels. This allows reduction of experimental variables, so that a lengthy programme of screening experiments is avoided.

In this work suitable preparation conditions of PVDF/PPy composite membranes were determined, based on obtaining high conductivity and water flux for the resulting membranes. At least three samples were prepared for each test.

The conclusion from this part of the program was that:

(1) Water flux is less sensitive to the three variables than conductivity.
(2) Reactant concentration has the most impact on both conductivity and water flux.
(3) Temperature has a significant but smaller effect on conductivity.

From this phase of the program it was found that suitable conditions after 15 min exposure to 1.2 M pyrrole at 0°C, followed by a similar exposure to 3 M $FeCl_3$. These results are consistent with other researchers' work in this area. For example, Liang *et al.* have shown that PPy perchlorate chemically synthesized at 0°C is more conductive due to a higher doping level, lower defect sites and longer conjugation length[19], than at higher temperatures. Similar optimized conditions were also found for the polymerization of pyrrole by Yamaura *et al.*, when methanol was used as solvent for the oxidant[20].

Modified composite membranes

Sulfonated additives were incorporated into PPy either during polymerization or subsequent post-treatment. Various anion dopants including low molecular weight and polymeric surfactants were used in addition to the oxidant. Two step chemical polymerization was carried out to prepare these composites. Polymerization conditions took into account the optimization experiments for unfunctionalized composites.

For low molecular weight surfactants including the sodium salt of dodecyl benzene sulfonic acid (DBS), chlorosulfonic acid (CSA) and low molecular weight dopants including tetraethyl ammonium *para*-toluene sulfonate (TEA*p*TS) and *para*-toluene sulfonic acid (PTS), the following conditions were used.

Oxidant concentration:	3 M
Monomer concentration:	1 M
Doping agent concentration:	0.3 M
Polymerization temperature:	0°C
Exposure time to monomer/dopant and to oxidant solution:	15 min

10 wt% aqueous solutions of polymeric dopants including the sodium salt of polyvinyl sulfonic acid

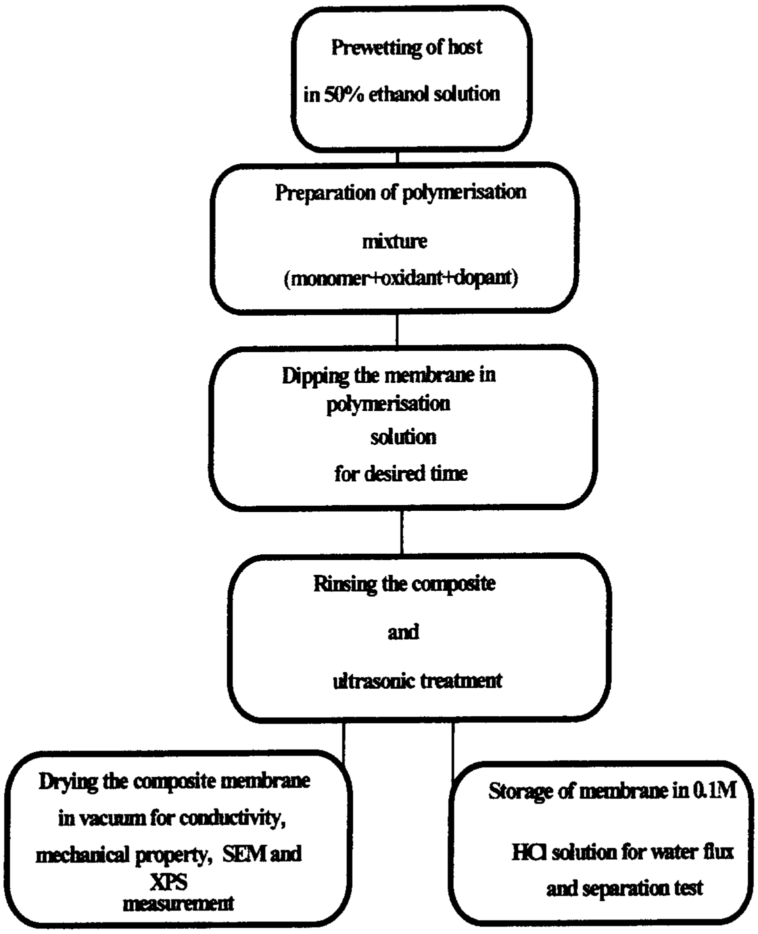


Figure 2 Preparation of composite membrane by the one-step method

(PVSNa) and the potassium salt of polyvinyl sulfate (PVSK) were also used as dopants.

Untreated membranes were first dipped in a mixed solution of dopant and monomer and then in the oxidant solution. Dopants were also incorporated into the membrane at the post-treatment stage, by dipping the unfunctionalized conducting membranes in dopant or surfactant solution.

One step polymerization

This technique was trialed, on the basis of the successful preparation of polyaniline reported by Kaner and McDiarmid[21]. This route was confined to low reactant concentrations. Polymerization and coating were carried out in a simple one-step method. The host membrane was dipped in a continuously stirred mixture of freshly distilled pyrrole (0.02 M), ferric chloride (0.01 M) and the sodium salt of anthraquinone-2-sulfonic acid (AQSA) (0.08 M) at 0°C (see *Figure 2*).

RESULTS AND DISCUSSION

Morphology

Satisfactory functioning of the conducting composite membranes needs coatings which are even to achieve consistent performance and are thin to allow high flux and permeability.

The top surfaces of untreated and treated hydrophobic PVDF membranes (GVHP) are shown in *Figures 3a* and *3b*. Pore size is barely reduced. This is crucial as high porosity needs to be retained for good flux performance. Secondly, there is some surface roughening, consistent with typical nodular or cauliflower morphologies reported for free standing films (for example see ref. 22). This change in texture is sufficiently pronounced to allow differentiation between PVDF and PPy, not sufficiently convoluted to reduce membrane performance via fouling. Finally, there are also numerous aggregates and individual particles of colloidal PPy, which are reduced in number and size after ultrasonic treatment. Similar contamination with particulate PPy has been found for PC membranes[23].

Micrographs of freeze-fractured cross sections of untreated and treated PVDF membranes (*Figure 4*) shows that PPy persists throughout the whole section, as shown by the roughness of pore walls throughout and by the presence of some PPy particles below the surface.

An EDA SK_α line scan of *p*-toluene sulfonate doped PPy analysis for sulfur is shown in *Figure 5* and indicates, assuming exclusive dopant to PPy association, that PPy persists throughout the section. This indicates that PPy is coating pores throughout the membrane. Whilst this appears to be rather thin, as indicated by FESEM, and so flux is not diminished significantly, other properties related to surface chemistry/charge may be changed significantly.

Electrical conductivity

Unmodified system. Conductivities up to 4.8 S cm^{-1} were obtained for samples prepared under optimum conditions, with the average conductivity in the range of 2.1 ± 0.6 S cm^{-1} (mean of 30 samples). The PPy weight uptake of PVDF membranes was found to be 7.8 ± 1.2% (10 samples).

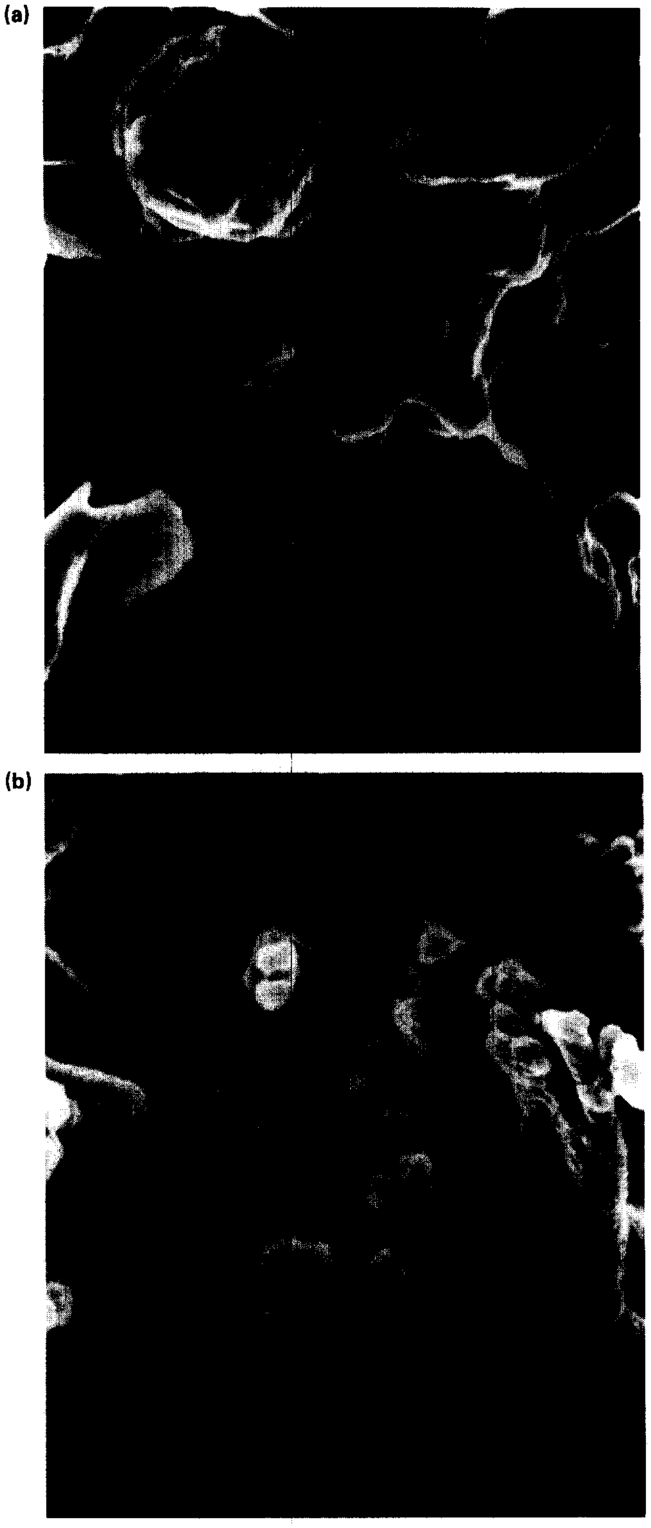


Figure 3 Surface morphology of (a) GVHP and (b) GVHP/PPy composite membrane

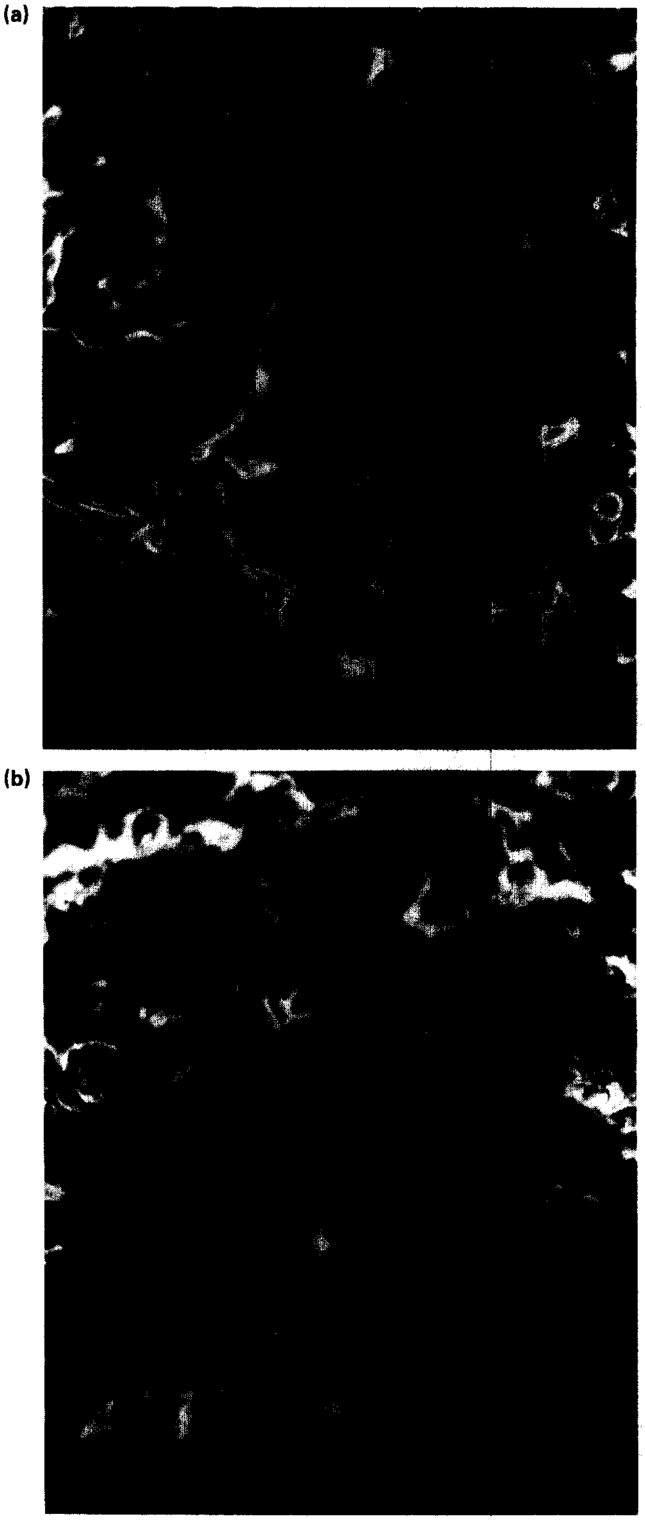


Figure 4 Cross section of (a) GVHP and (b) GVHP/PPy composite membrane

Modification of composite membranes by the two step method

The main aim of functionalizing conducting composites is stability improvement, particularly in wet conditions.

Table 1 summarizes the conductivities of modified systems. Composites with various conductivities can be obtained by variation of dopants and the method of preparation. In general, incorporation of low molecular weight dopant causes a modest reduction of intial conductivity. The lowest conductivity ($0.5\,\mathrm{S\,cm^{-1}}$) was obtained when *p*-toluene sulfonic acid was used as dopant, while for the polymeric dopant the initial conductivity is comparable with non-dopant treated composite membrane (i.e. in the range $3-5\,\mathrm{S\,cm^{-1}}$). When composites were functionalized with a low molecular weight surfactant (dodecyl benzene sulfonic acid, sodium salt) the initial conductivity is $1.3\,\mathrm{S\,cm^{-1}}$.

One-step polymerization method

These composites were prepared by one step method using the sodium salt of anthraquinone-2-sulfonic acid

Table 1 Modified conductive composite membranes

Sample	Sample code	Incorporated dopant	Preparation comment	Conductivity ($S\,cm^{-1}$)
1	PVDF-PPy-TEA-F	Tetra ethyl ammonium *p*-toluene sulfonate	Ethanol solvent for monomer and dopant	0.5
2	PVDF-PPy-TS-F	Para toluene sulfonic acid	Normal condition	0.4
3	PVDF-PPy-TEAS-F	Tetra ethyl ammonium *p*-toluene sulfonate	Composites soaked in acidic dopant solution	4.5
4	PVDF-PPy-DBSA-F	Dodecylbenzene sulfonic acid	Normal condition	1.3
5	PVDF-PPy-CSAS-F	Chlorosulfonic acid	Composites soaked in dopant	2.6
6	PVDF-PPy-PVSNa-F	Poly vinyl sulfonic acid, Na salt	Composites kept in vacuum	3.5

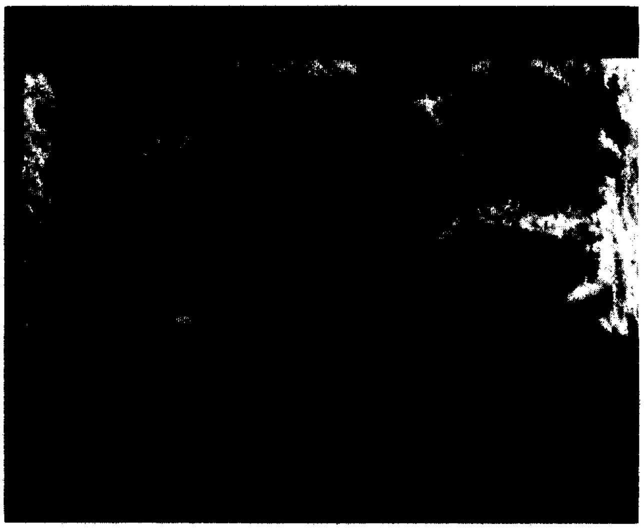


Figure 5 EDA of a cross-section of PVDF/PPy composite membrane, SK_{α} (2.31keV)

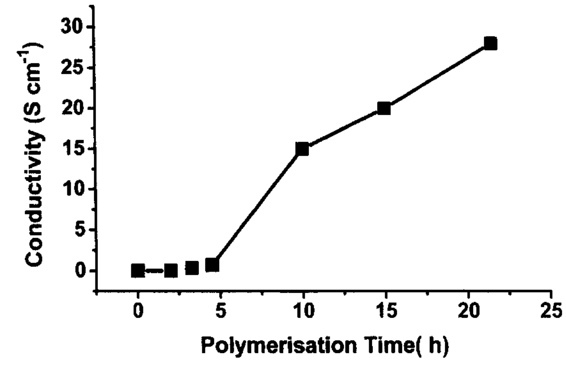


Figure 6 Conductivity vs polymerization time for PVDF/PPy composite membrane

(AQSA) as dopant. Polymerization time was changed and conductivity was measured (*Figure 6*). Conductivity of the composite increases slowly with polymerization time for the first 4 h and then increased linearly at a higher rate. The polymerization rate is lower than that for two-step preparation, probably due to the lower reactant concentration. The presence of an induction time was also reported by other researchers (for example see ref. 24).

Environmental stability

Unmodified composite membranes.

Ageing in protic acids: Composite members were stored in 0.01, 0.1 and 1 M H_2SO_4 (pH $\cong$ 1–2) and 0.1 M HCl solutions for extended times and conductivity was measured (*Figure 7*)[25]. Conductivity is retained and even enhanced over short periods. This effect is attributed partly to further protonation[11,26] and also to the anion exchange properties of conducting polymers[27]. In our work both effects were observed, as confirmed by X.p.s. experiments discussed later.

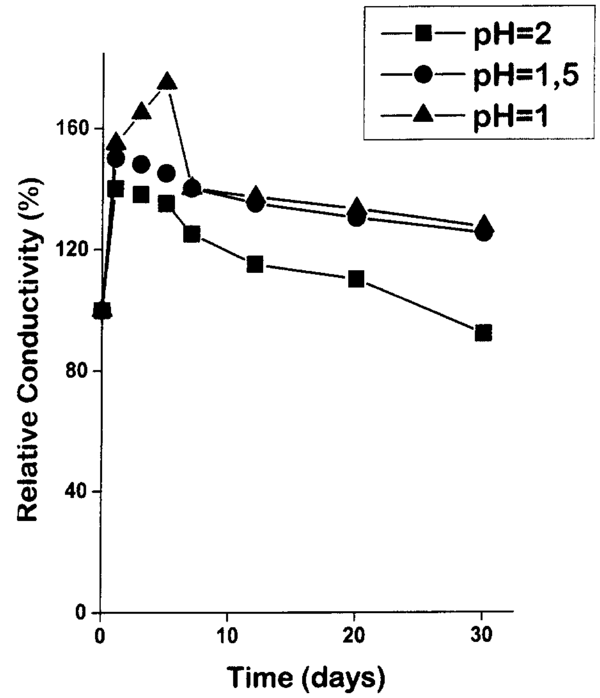


Figure 7 Relative conductivity of unfuntionalized conductive composite membranes in sulfuric acid[25]

Ageing in basic media: The ageing of composite membranes in NaOH solutions were also studied, with conductivity reducing quickly. Conductivity decreased from 3.1 $S\,cm^{-1}$ to 2.2 $S\,cm^{-1}$ within 5 s in 0.01 M NaOH, and after 20 min to 0.002 $S\,cm^{-1}$. Higher concentrations of NaOH accelerated this effect. X.p.s. studies revealed that the doping level (Cl^-/N) for NaOH treated samples is very small. This observation confirms that NaOH treatment has led to depletion of the dopant Cl^- ion. The higher oxygen content in base-treated samples might be considered as evidence for replacement of original dopant by hydroxide anion, which binds covalently to PPy[28]. These covalent bonds shorten the conjugation length and reduce the conductivity, as will be discussed later.

Stability in water and moderate ionic strength media: Conductivity decreased up to 40% in water after 14 days storage (*Figure 8*). After this period the conductivity

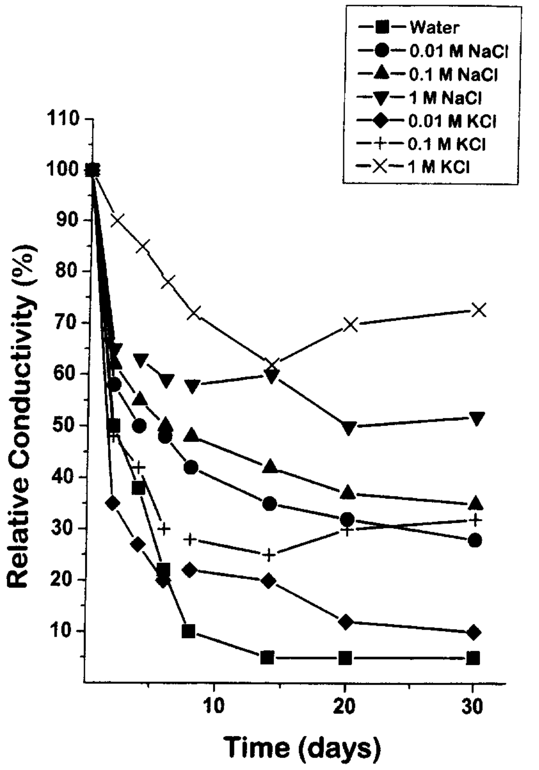


Figure 8 Conductivity decay in water and moderate ionic strength media[25]

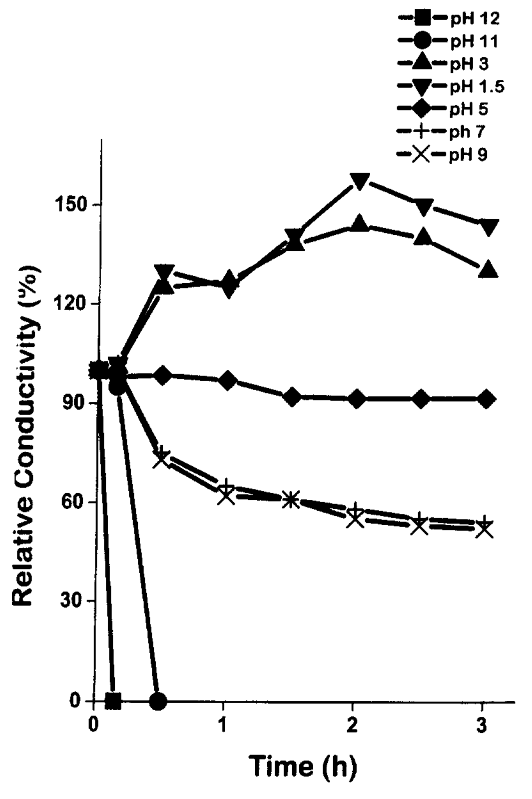


Figure 9 Effect of pH on conductivity of PVDF/PPy composite membranes

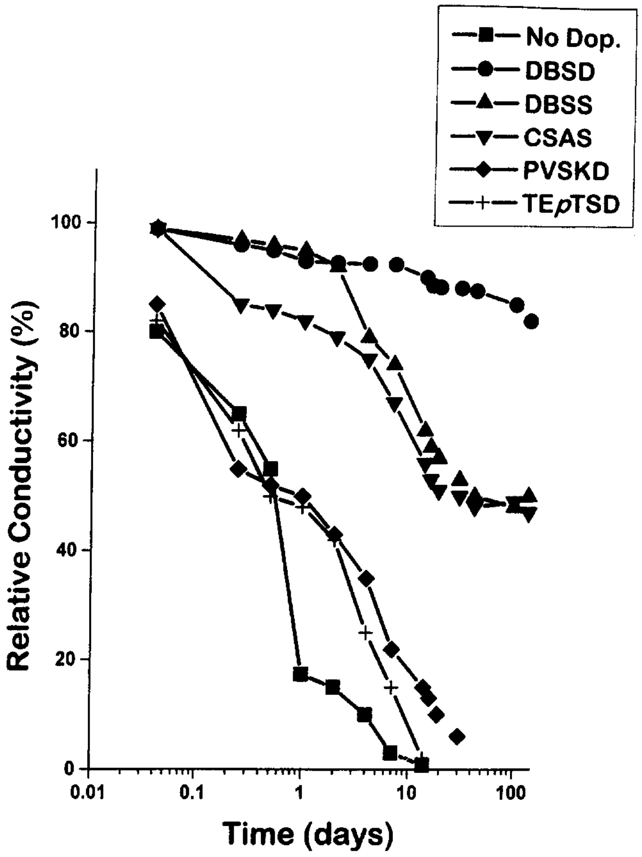


Figure 10 Conductivity decay of composite membranes in water before and after modification

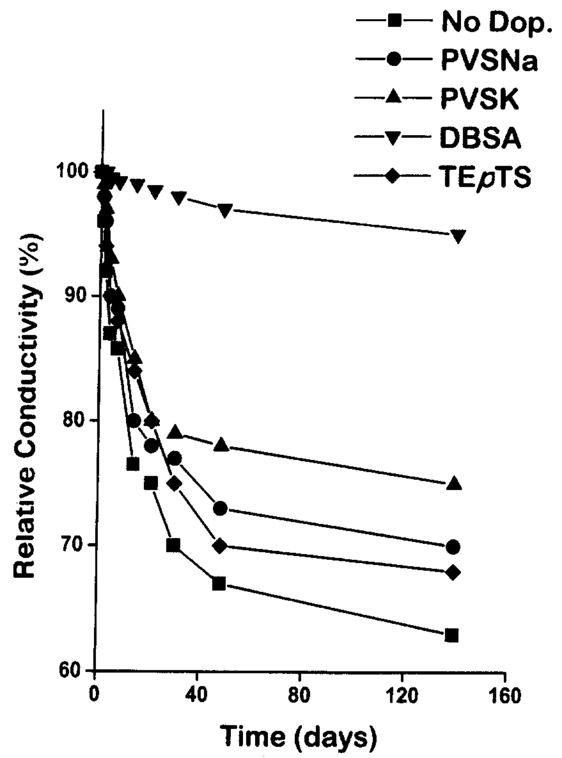


Figure 11 Conductivity decay of composite membranes in air before and after modification

decreased at a lower rate. Immersion in water imposes a significant effect on conductivity of composites. The main reason for this effect is nucleophilic attack by water producing hydroxyl bonding at the β-position. These bonds can be oxidized further to carbonyl ($>$ C=O) bonds (e.g. pyrrolin-3-one or pyrrolin-2-one in the case of initial attack at the α-position), which can cause chain scission[29]. However, addition of NaCl or KCl (common halide counterions) improved the

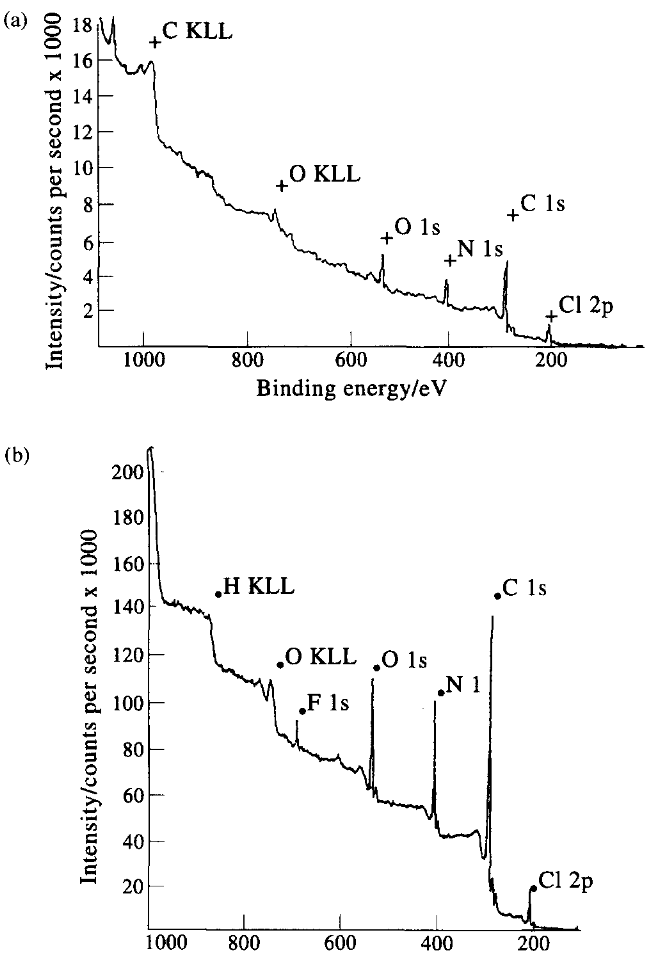


Figure 12 X.p.s. wide scan of: (a) chemically prepared PPy/$FeCl_3$ complex with an intial $FeCl_3$/monomer ratio of 3 in aqueous media; (b) PPy/PVDF/$FeCl_3$ composite membranes. Peaks are identified as fluorine (Fls), oxygen (O1s), nitrogen (N1s), carbon (C1s) and chlorine (Cl2p)

stability; samples stored in 1 M NaCl have retained their conductivity up to 50% after 1 month, and in KCl up to 70% for the same period of time, as shown in *Figure 8*.

Ageing in solutions with different pH: Solutions having different pH's (from 2 to 10) were prepared either from NaCl and HCl (in small amounts) or NaCl and NaOH (in small amounts). Aged samples were rinsed with water, dried with nitrogen gas and the conductivity was measured after different storage times (*Figure 9*). Composite membranes stored in solutions with lower pH (less than 4) retained their conductivity. However, the decay in solutions with the pH in range of 7–9 is significant, and for solutions with pH >10 is dramatic. Similar results were reported for PPy/*p*-toluene-sulfonate free standing film[30] and PPy/fabric composites[31].

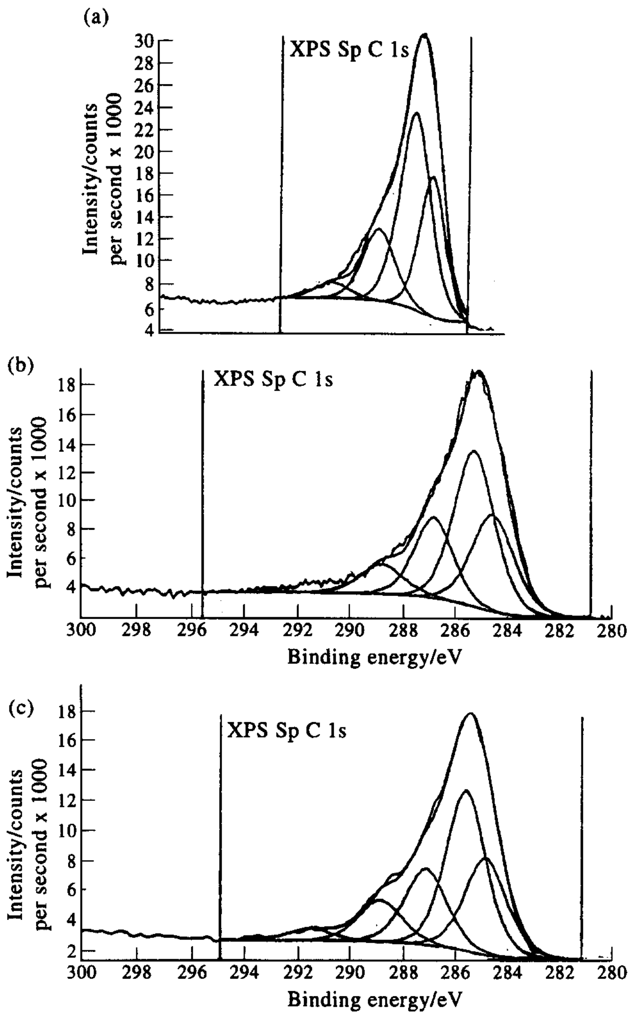
Stabilization. As demonstrated earlier, by changing the environment to either a lower pH or a higher ionic strength, the stability of conducting membranes can be enhanced, but in a real application these variables may not be controllable. An alternative approach is to improve the inherent stability by functionalizing conducting polymers with, for example, sulfonated dopants and surfactants. This approach was used by incorporating sulfonated additives either during polymerization or subsequent post-treatment.

When composites were functionalized by a low molecular weight surfactant, there was a significant improvement in stability in water and air (*Figures 10* and *11*). The most stable treated membrane was that in which the sodium salt of dodecyl benzene sulfonic acid was present. In this case the initial conductivity is still rather high ($1.3\,S\,cm^{-1}$) but the main benefit is that it can be maintained in service. Replacement of Cl^- (as discussed below) by sulfonate might be one reason for this improvement. In addition, since DBSA is a polar molecule, it will bind to PPy (a polar polymer). This may induce a change in the polypyrrole molecular conformation and might lead to a higher crystallinity and thus higher stability. It was also reported that dopant-incorporated PPy films have relatively smooth surface morphologies, which inhibit oxygen penetration[32].

Table 2 X.p.s. surface compositional data for the selected samples

Sample	Sample code	Preparation/treatment comments	Conductivity ($S\,cm^{-1}$)	Chemical composition	Doping ratio
1	PPy [3/1]	Polypyrrole powder prepared chemically	12	$C_{4,6}$ N $Cl_{0.33}$ $O_{0.76}$	0.37
2	PVDF-PPy	Two step polymerization onto the substrate	3.8	$C_{4.4}$ $Ncl_{0.21}$ $O_{0.70}$	0.21
3	PPy-PVDF-W	Composites aged in water	2.5	$C_{4.5}$ $Ncl_{0.16}$ $O_{0.55}$	0.16
4	PPy-PVDF-B	Composites aged in 1 M NaOH	10^{-4}	$C_{4.9}$ $Ncl_{0.03}$ $O_{1.14}$	0.03
5	PPy-PVDF-S3	Composites aged in 1 M H_2SO_4	4.5	$C_5NCl_{0.0008}(SO_4)_{0.03}$ $O_{1.36}$	0.13
6	PVDF-PPy-TEA-F	Solvent for monomer and dopant is ethanol	0.5	–	0.34
7	PVDF-PPy-sTEA-F	Composites soaked in acidic solution of dopant	4.5	–	–
8	PVDF-PPy-DBSA-F	–	1.3	–	0.31
9	PVDF-PPy-DBSA-W	No 8 aged in water	1.0	–	0.17
10	PVDF-PPy-sCSA-F	Composites soaked in dopant	2.6	–	–
11	PVDF-PPy-PVSNa-F	Composites kept in vacuum	3.5	$C_{4.8}$ $NCl_{0.3}(SO_3)_{0.05}$ $O_{0.85}$	0.45
12	PVDF-PPy-PVSNaW	No 11 aged in water	1.1	$C_5NCl_{0.34}(SO_3)_{0.06}$ $O_{0.97}$	0.35

For polymeric dopants (PVSK) the initial conductivity is somewhat higher than low molecular weight dopants (in the range $3–5\,S\,cm^{-1}$), but the retention of conductivity is low. Whilst studies of closely related materials in water have not previously been reported, there is relevant evidence for composite textiles[31]. Here higher stability is related to reduced amounts of retained chlorine ion. This correlates well with the present findings.



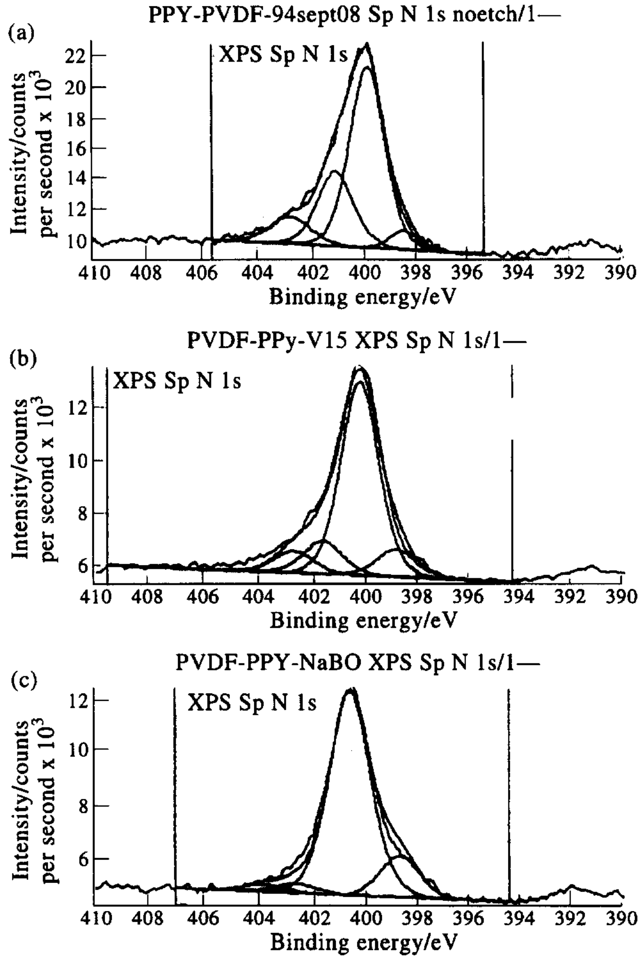
	Concentration		
Chemical State	Untreated	Aged in water(2 weeks)	Aged in base(< 1hr)
βC	29.1	27.7	25.3
αC	48.9	42.7	40.2
C-O	17.9	21.0	20.0
C=O	4.1	8.6	11.2
O-C=O	<0.5	< 1	3.2

Figure 13 C1s X.p.s. core-level spectra for composite membranes: (a) untreated; aged in (b) water; and (c) base

X-ray photoelectron spectroscopy studies. The X.p.s. wide scan of the surface of composite membranes show peaks corresponding to the constituent elements of PPy, with some modest contribution from the substrate. *Figure 12* shows a typical X.p.s. spectrum for PPy powder and composite membranes of PPy with microfiltration PVDF membrane, respectively. The area which was scanned was about 12 mm^2.

Table 2 summarizes conductivity, chemical composition and doping ratio for samples prepared under different conditions. Doped PPy should ideally have the empirical formulae $C_4H_3NX_n$, where X is the dopant or dopants counterion and '*n*' is the fractional doping level. X.p.s. determination results for untreated PPy (sample No. 1) are in good agreement with other PPy/$FeCl_3$ complexes prepared under similar conditions[19]. However, all quantitative X.p.s. analyses show a systematic carbon excess, especially after brief etching, which may be derived from different sources. For the unmodified PPy powder control, this can be attributed to surface hydrocarbon contamination, as observed by other researchers[33]. For composites and modified samples, this might also be partly due to contributions from substrate and/or dopants.

The composition analysis (*Table 2*) reveals the presence of oxygen in all samples, as observed in other chemically[34] and electrochemically[35] prepared PPy. This excess oxygen can be attributed to surface oxidation products, and also due to PPy reaction with water as synthesis solvent[29].



	Concentration		
Chemical State	Untreated	Aged in water(2 weeks)	Aged in base(< 1hr)
>C=N-	4.9	10.0	15.0
-NH	59.6	69.3	78.6
N+	25.4	13.0	3.5
N++	10.1	8.1	2.8

Figure 14 N1s spectra for composite membrane of PVDF/PPy before (a) and after exposure to water (b) and excess base (c)

The results presented in *Table 2* show the oxygen content in the range of 0.5–0.9 for non-hybridized systems. Ion etching of samples showed an increase in carbon content and in most cases a large decrease in oxygen content. A decrease in oxygen content is due to the removal of oxidized species (e.g. C–O, C=O bonds).

Unmodified systems

C1s. For unmodified systems $FeCl_3.6H_2O$ was used as oxidant and no extra dopant was added. The broadness of C1s peak indicates carbon–carbon bonds and carbon–oxygen bonds at higher binding energy. For the ideal polypyrrole system, the only carbons which should exist are α-carbons and β-carbons: however due to oxidation there are oxidized carbon species including carbonyl (–C=O, C–O (e.g. C–OH and hydroperoxide)), which causes a shoulder at high binding energy[36].

The C1s spectra for composites of PPy and PVDF before and after ageing in water and alkaline solutions are shown in *Figure 13*. The FWHM was kept constant for all of the component peaks. The percentage ratio of each component (α-carbons, β-carbons and oxidized carbons) is shown in the corresponding table, which provides peak assignments for lower binding energy (284 eV for αC) to higher values. The C1s of this sample has a similar shape to that of PPy alone. The αC and βC peaks for samples aged in water have a lower intensity and peaks related to disorder carbon are stronger, suggesting higher degrees of oxidation. The lower C–O/C=O ratio for this composite compared to an untreated sample (2.4 vs 4.5) can be attributed to conversion of more C–O species to C=O species.

Figure 13c shows the X.p.s. C1s for a sample treated with excess NaOH, with an increase in the shoulder peak at high binding energy being observed. The αC and βC contributions are reduced relative to the total

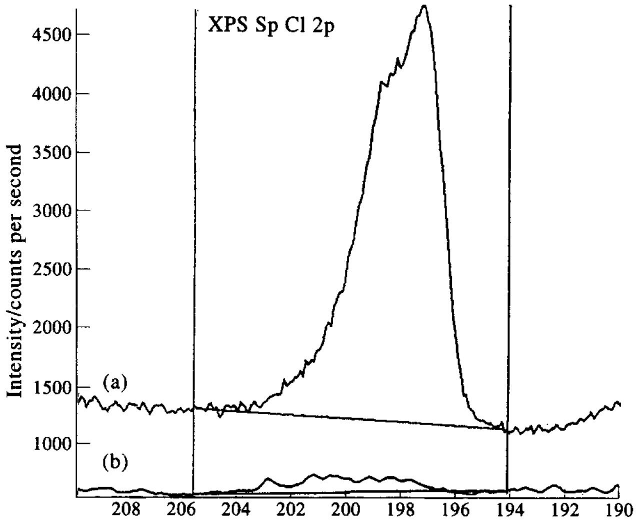
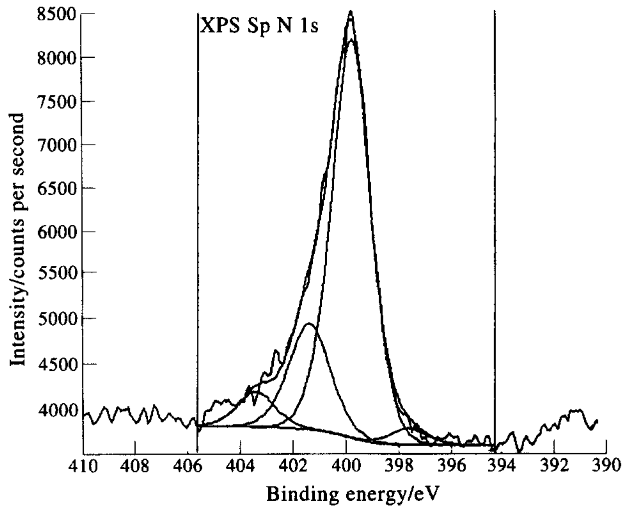


Figure 15 The Cl X.p.s. core-level for: (a) PVDF-PPy-F, 'Fresh'; (b) PVDF-PPy-B, 'Base treated', indicating the effect of base treatment



Chemical state	Concentration
-NH	71.4
N+	19.7
N++	6.0
>C=N-	2.8

Figure 16 N1s core-level spectra of composite membrane of PVDF/PPy after treatment with 1 M H_2SO_4

carbon amount, indicating some oxidation on the α carbon site as well as the β carbon site. This increase in C=O concentration reveals that some, preferentially β carbons, have been fully oxidized by bases, leading to ring cleavage. A more interesting point about this sample is the appearance of another peak at a higher binding energy (291.2 eV). This can be assigned to the hydroxylic species[18], indicating that further oxidation has occurred. The degree of oxidation is about 35%, consistent with the results presented in *Table 2*.

N1s. N1s X.p.s. spectra for untreated composites and samples aged in water and alkaline solutions are shown in *Figure 14*. The main one at about 400.65 eV is attributed to the neutral pyrrolylium (amine) nitrogens. The two high binding energy peaks (shoulder peaks) are attributed to nitrogens with a partial positive charge $((-N^+ + N^{++})/N)$[37,38]. There is also a small, but

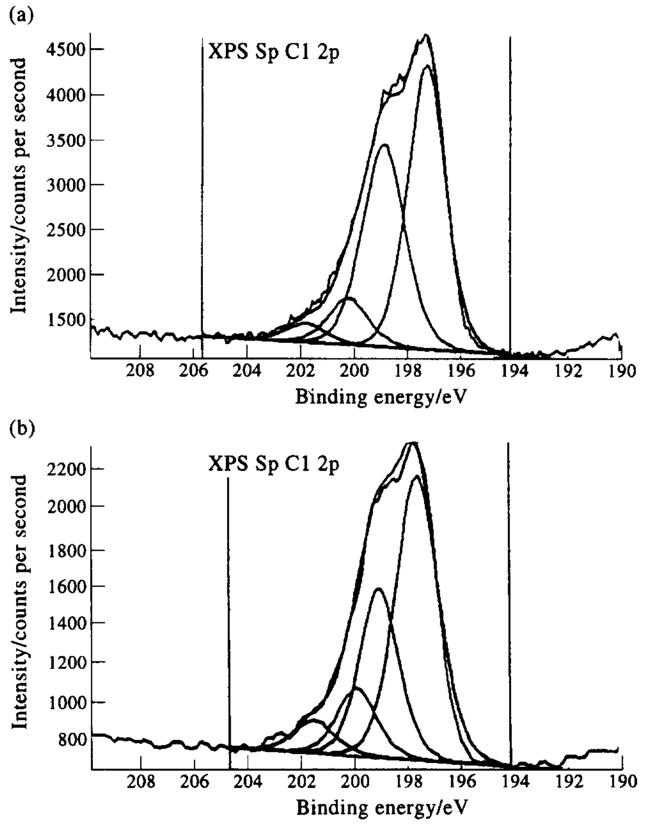


Figure 17 Cl2p core-level spectra for PPy (a) and PVDF-PPy composite membrane (b)

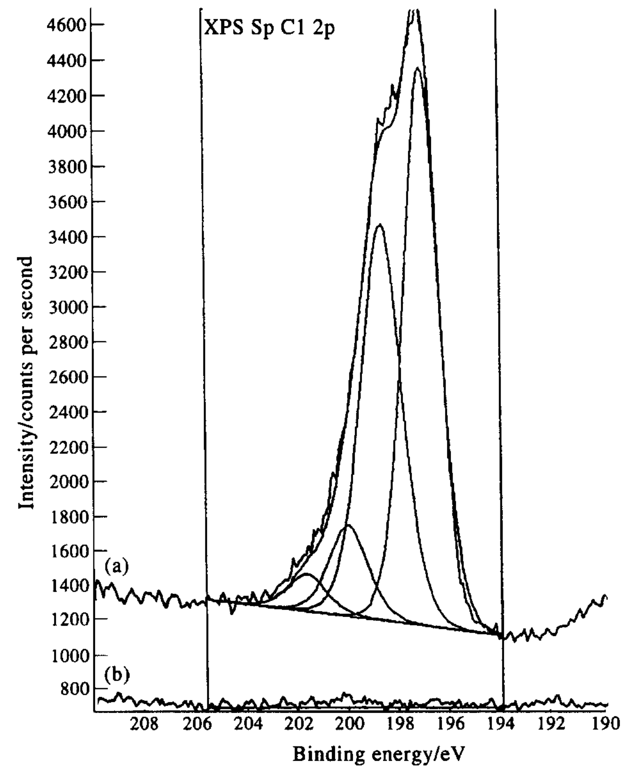


Figure 18 Cl2p core level spectra of composite membrane treated with 1 M H_2SO_4 (b) as compared with the untreated sample (a)

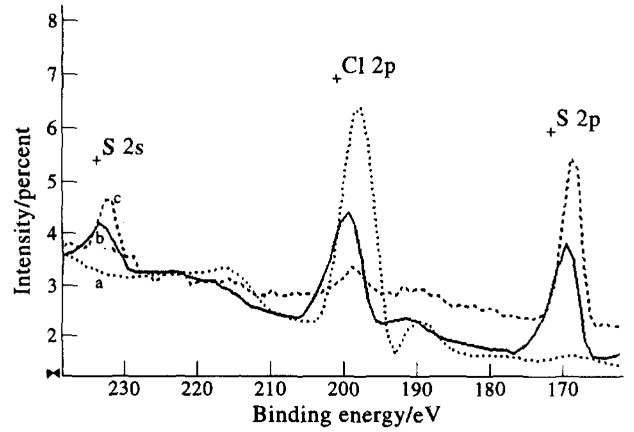
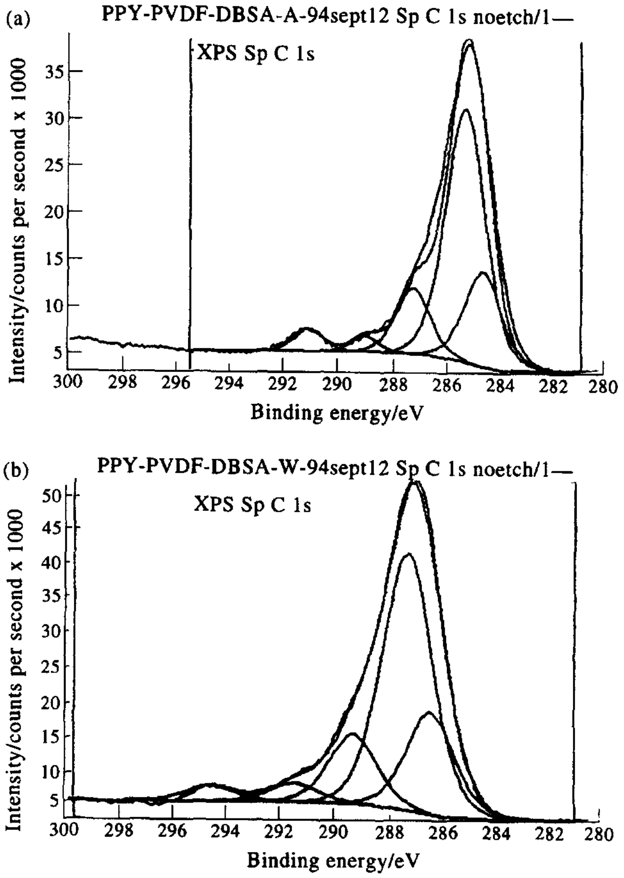


Figure 19 X.p.s. wide scan of unmodified (PVDF/PPy) (a) and modified systems: (b) PVDF-PPy-PVSNa; (c) PVDF/PPy/DBSA

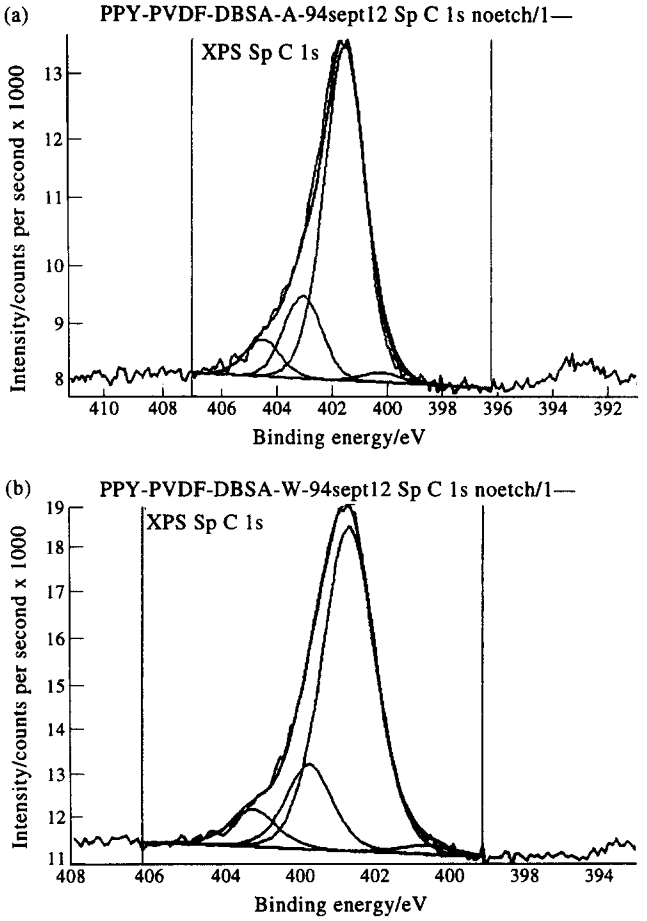


	Concentration	
Chemical state	Untreated	Aged in water(2 weeks)
βC	21.2	21.6
αC	59.3	56.5
C-O	13.2	14.6
C=O	2.5	3.9
CF_2	3.8	3.3

Figure 20 Cls X.p.s. core-level for: (a) PPy-PVDF-DBSA-F; (b) PPy-PVDF-DBSA-W

clearly resolved low binding energy shoulder at 398.5 eV, which has been attributed to deprotonated, uncharged, imine-like nitrogens (>C=N–) formed upon dehydrogenation of a fraction of the pyrrolium nitrogens[37]. N1s spectra for samples aged in water (*Figure 14b*) shows up to twice the intensity of the low binding energy should, as well as a decrease in the intensity of the high binding energy shoulder, indicating partial deprotonation of some –NH species. This effect is more severe for base-treated composite membranes, with *Figure 14c* showing the N1s core-level spectra of PVDF-PPy composite surface after treatment with NaOH (pH = 12). The number of positively charged nitrogens are reduced to one sixth and one fourth of that of untreated and water aged samples, reflecting an almost complete loss of the Cl2p anion signal (*Figure 15* and *Table 2*). This again verifies that ionic chlorine is associated with a specific nitrogen cation. The low binding energy shoulder (> C=N–) for this sample has a higher intensity. The > C=N– defect is important, as this interrupts conjugation, leading to shorter conjugation lengths, longer hopping lengths, and thus lower conductivity.

Treatment of PVDF-PPy-W with 1 M H_2SO_4 results in reprotonation and anion exchange. The low binding



	Concentration	
Chemical State	Untreated	Aged in water(3 weeks)
>C=N	1.8	1.9
-NH	74.2	73.5
N+	16.8	17.1
N++	7.1	7.5

Figure 21 N1s X.p.s. core level spectra for: (a) PPy-PVDF-DBSA-F; (b) PPy-PVDF-DBSA-W

energy shoulder associated with deprotonated pyrrolium nitrogens has diminished substantially. This is readily correlated with the appearance of an appreciable amount of the S2p core-level in a wide scan spectrum signal and the positively charged nitrogens in the N1s core-level spectrum (*Figure 16*).

Cl2. The Cl2 peak is a typical chlorine doublet from the 2p3/2 and 2p1/2 subshells (peak separation was maintained at 1.6 eV). These doublets in PPy systems have been resolved into either two[14] or three[34] components. Makhlouki *et al.* assigned the Cl2p for PPy/poly(vinyl alcohol) composites into a two spin-orbit split for each of the doublets suggesting two distinct chemical states, including ionic (Cl^-) at a lower binding energy and covalent (–Cl) at a higher binding energy[14].

The Cl2p core-level spectra for the various systems in the present study have slightly different line shapes. *Figure 17* shows the respective Cl2p core-level for the chemically prepared PPy and PVDF/polypyrrole composites aged in water. The Cl2p for PPy powder and composites of PPy and membranes is well deconvoluted into two-spin-orbit-split doublets, indicating that incorporated chlorine exits in two distinct chemical states. Low binding energy peaks are assigned to anionic species including Cl^-2p3/2 and Cl^-2p1/2 and high binding energy peaks are assigned to corresponding covalently bound chlorine bonds. For curve fitting the separation between the two doublets is kept at about 1.6 eV and the separation between ionic and covalent peaks kept at about 2 eV.

Treatment of the composite membrane with 1 M NaOH results in the loss of chlorine anion, as shown in *Figure 15* where the corresponding Cl core-level spectra of PVDF-PPy- and PVDF-PPy-B are shown. The very small amount of chlorine in the latter sample could be attributed to the remaining covalent chlorine species. This is accompanied by a loss of the N1s high binding energy tail (attributable to the N^+ component) and the appearance of the deprotonated pyrrolylium nitrogens, as mentioned before. Immersion of composite membranes in 1 M H_2SO_4 also led to almost complete depletion of chlorine species (*Figure 18*). The appearance of sulfur in wide scan X.p.s. spectra confirmed the anion exchange processes for this sample.

Anion exchange behaviour of conducting composite

Modified conductive composite membranes. Two modified systems were studied by X.p.s. The extra dopant in these systems, which are designated as (PPy-PVDF-DBSA) and (PPy-PVDF-PVSNa), were sodium salt of dodecylbenzene sulfonic acid, and sodium salt of poly(vinyl-sulfonic) acid, respectively.

Both chlorine and sulfur are incorporated in these systems (*Figure 19*) compared with the non-modified system. However the concentration of chloride for PPy-PVDF-DBSA is almost one-sixth that of sulfur, while for the polymeric dopant this ratio is 0.74. That means that a lower amount of residual chloride is present in those composites which exhibit the highest stability. Since polymerization is carried out by oxidative coupling using a high concentration of $FeCl_3$ (3 M), copious amounts of Cl^- are available during polymerization. However, sulfonate dopant has still replaced the chlorine ion, to give higher stability of the system in air and water. Kuhn *et al.*[39] and Heisley *et al.*[40] have reported similar results for conductive textiles where, in the latter case, no significant chlorine was measured, while about 1% of sulfur was detected.

The C1s of PPy-PVDF-DBSA is shown in *Figure 20*. There is a well resolved peak at higher binding energy (~291 eV), which can be assigned to CF2, which arises from the substrate. This, together with the presence of a fluorine peak in the wide scan spectrum and a high C/N ratio (~9.4) suggest that either some parts of membrane remain uncoated or the coating is very thin in this case.

The C1s and N1s spectra for this sample remained almost unchanged after ageing in water for 2 weeks, as shown in *Figures 20* and *21*. These results which reflect the higher stability of this sample in water suggest that the chemical structure remained unchanged upon ageing. An interesting point about the N1s peak is the low concentration of the lower binding energy peak which has been assigned to the deprotonated (>C=N) species. As was shown before, this was 5% for the unmodified control system, which increased to 10% after aging in water. This again verifies that a higher quality polymer has been obtained by using the sulfonated surfactant.

CONCLUSIONS

PPy-PVDF composite membranes have been analysed by X.p.s., FESEM, microprobe analysis and conductivity measurements as a function of storage time in different media. Morphological studies showed that the microfilter pore size is only slightly reduced upon coating the conducting polymer. The main focus of this work was to study the chemical structural changes upon ageing in air and aqueous environments. These studies showed that oxidation of aged samples occurs on the α carbon as well as the β carbon. For some aged samples further oxidation was occurred as was shown by the appearance of a peak at high binding energy (~290 eV) in the C1s core level spectra.

Dopant depletion was found to be the other major reason for conductivity loss upon ageing. Finally it was shown that by incorporation of sulfonated additives the inherent stability of composite membranes can be improved. The most modified membrane was that in which sodium salt of dodecyl benzene sulfonic acid was used. This was assigned partly to the replacement of chlorine by sulfur and partly to the lower amount of deprotonated nitrogen.

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