Oxidation and ion migration during synthesis and degradation of electroactive polymer–nylon 6 composite films

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Abstract

In the synthesis of polyaniline–nylon 6 composite films wherein the polymerization was carried out by the immersion of aniline-containing nylon 6 films in an acid solution which has an oxidant ($(NH_4)_2S_2O_8$), the polymerization time has to be carefully monitored to prevent over-oxidation of the polyaniline. This method is likely to yield polyaniline in the protonated pernigraniline (rather than the emeraldine) state which undergoes hydrolysis in the acidic medium. Polyaniline–nylon 6 composite films with Cl^- are converted to the base form as the counter-ions readily lose the Cl^- anions when immersed in water. In contrast, the use of sulfosalicylic acid (SSA) as the protonic acid yields composite films which do not convert to the base form after extended exposure to water or under simulated weathering conditions. In the synthesis of polypyrrole–nylon 6 composite films, a substantial amount of polypyrrole can be readily formed in the nylon 6 matrix resulting in the destruction of the crystalline structure of the nylon 6 film and a large decrease in tensile strength. A significant amount of the iron chloride used as oxidant is also retained in the film causing blackening of the film under heating or simulated weathering. The removal of iron chloride from the film is not readily achieved by immersing the film in water but more so in SSA. The SSA anions also lend a greater degree of stability to the film upon exposure to water. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline–nylon 6 composite films; Polypyrrole–nylon 6 composite films; Oxidation

1. Introduction

The electrically conductive polymers, polyaniline (PANI) and polypyrrole (PPY), have been considered as good candidates for commercial applications because of their ease of synthesis, relatively high electrical conductivity and stability in air. However, the PANI and PPY films often lack mechanical strength, and increasing efforts have been directed towards circumventing this problem. For example, the preparation of cross-linked PANI films from gels [1,2] has been found to result in better mechanical properties than those obtained from typical dilute solutions. Alternatively, the problem of low mechanical strength can also be overcome by adhering the conducting polymers to strong flexible textile substrates [3], or by the synthesis of composites of PANI and PPY with other polymers [4–7].

A simple method widely used in the synthesis of PPY or PANI composites involves a first step of containing either the oxidant [4] or the monomer [5–7] within a conventional polymer matrix. In the second step, the oxidant-containing or monomer-containing polymer matrix is exposed to the monomer or oxidant solution, respectively, to initiate the polymerization reactions within the conventional polymer matrix. This diffusion–oxidation technique results in a reaction front which progresses into the polymer matrix. However, under such circumstances the conditions may not be optimal for the polymerization reactions. For example, when the aniline or pyrrole monomer-containing polymer matrix is placed in the oxidant solution, the polymerization reactions will start at the interface in contact with the oxidant solution. As the oxidant diffuses into the matrix and the polymerization continues inside the polymer matrix, the PANI or PPY formed initially is continually exposed to the oxidant solution. This may result in the degradation of the PANI or PPY. The unreacted reactants and by-products of the polymerization reaction may also be trapped in the matrix.

In the present work, we report our investigations on the synthesis of PANI–nylon 6 and PPY–nylon 6 composites. Particular attention was directed at the aforementioned oxidation and ion migration processes during the synthesis and degradation of the composite films in water, under heating in air and under simulated weathering. The composite films were characterized by bulk analytical techniques as well as spectroscopic techniques.

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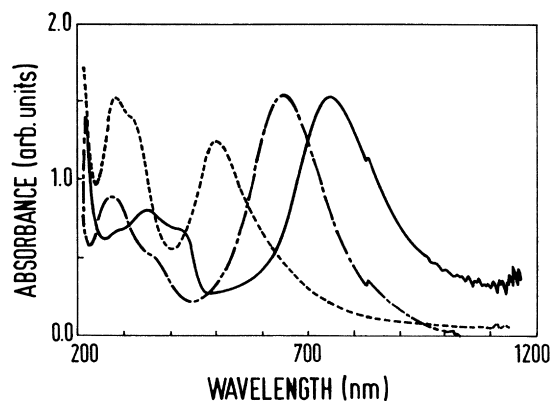*E-mail address:* chenkg@nus.edu.sg (K.G. Neoh)

Fig. 1. UV–visible absorption spectra of PANI–nylon 6 films immediately after 10 min of polymerization reaction (— · —); after 30 min quenching with deionized water (– –); and after 30 min reprotonation with 2 M HCl (film PA1) (—).

2. Experimental

2.1. Preparation of composite films

Nylon 6 films of thickness 0.015 mm were obtained from Goodfellow Inc. of UK. The as-received films were thoroughly washed with deionized water followed by methanol, and then dried under reduced pressure. The composite films were prepared using the published method [5] with some modifications. The nylon 6 films were first soaked in either aniline or pyrrole monomer for 1 h. The film was then blotted dry with filter paper to remove the residual monomer on the film surface. The aniline-containing film was soaked in a 2 M HCl solution containing 0.25 M $(NH_4)_2S_2O_8$ for varying periods of time (polymerization step). In the case of the pyrrole-containing film, a 2 M $FeCl_3$ solution was used. The polymerization reaction was terminated by the removal of the film from the oxidant solution and washing of the film with deionized water (quenching step). In the case of the PANI–nylon 6 composite film, a reprotonation step in which the water-washed film was placed in 2 M HCl solution was carried out. The composite films were pumped dry under vacuum before being subjected to further testing.

2.2. Stability tests

The composite films were subjected to stability tests in water, under heating and under simulated weathering. The water stability tests were conducted with the film being immersed in deionized water at 25°C for varying periods of time while the heat stability tests were carried out in an air circulated oven maintained at 80°C. The simulated weathering tests were carried out in a Xenon Weather-Ometer Ci 3000 (Atlas Electric Device Co). The weather chamber was maintained at a relative humidity of 70% and a dry bulb temperature and black panel temperature of 42 and 63°C, respectively. The irradiation directed at the film surface simulated solar irradiation with an intensity of

0.47 W/m^2 at 340 nm. For each 30 min test cycle, a water spray of 5 min duration was activated.

2.3. Film characterization

The tensile strength of the films was measured using a microprocessor-controlled material tester, Instron 5544. For each tensile strength reported, at least two measurements were taken and an average value calculated. The electrical resistance of the films was measured using the two-probe method, and expressed as Ω/sq [8].

The bulk elemental analysis for C, H, N, S was carried out using a Perkin–Elmer Series II CHNS Analyzer. The Cl content was determined by burning the sample and absorbing the resulting Cl in the combustion gas in a mixture of NaOH and H_2O_2 in water, followed by the titration for Cl [9]. The Fe content was determined by first digesting the films in aqua regia and using inductively coupled plasma spectrometry (ICP, Optima 3000DV from Perkin–Elmer). The X-ray photoelectron spectroscopy (XPS) analysis of the surface composition of the films was carried out using a VG ESCALAB MkII spectrometer with the films mounted on the standard VG sample studs by means of double sided adhesive tape. The conditions of the tests were similar to those reported earlier [10]. The ultra-violet (UV)–visible absorption spectroscopy analysis of the films was made using a Shimadzu UV 3101PC scanning spectrometer. The reference used was pristine nylon 6 film and the wavelength was scanned from 200 to 1200 nm.

3. Results and discussion

3.1. Polyaniline–nylon 6 composites

The UV–visible absorption spectra of the PANI–nylon 6 composite film obtained after 10 min of polymerization in the oxidant solution, followed by the quenching and reprotonation steps are shown in Fig. 1. The spectrum obtained immediately after 10 min of polymerization in the oxidant solution is not typical of that of emeraldine (EM, 50% oxidized PANI) salt, but rather protonated pernigraniline (fully oxidized PANI) with strong bands at 620 and 280 nm and a very weak absorption band at 320 nm as a result of the formation of the bipolaron lattice [11]. After the quenching step, the spectrum showed absorption bands at 520, 320 and 280 nm, which have been reported for neutral pernigraniline base [11,12]. The first absorption band at 520 nm is attributed to the transition from the valence band to the conduction band while the 320 and 280 nm bands are caused by the π–π* transitions centered on the benzenoid and quinoid rings, respectively [11]. The spectrum after the reprotonation step shows absorption bands at 340, 420 and 750 nm characteristic of EM salt [13,14]. However the presence of the sharp band at 750 nm attributable to interchain excitations in the doped salt, rather than the presence of a long absorption tail extending into the IR
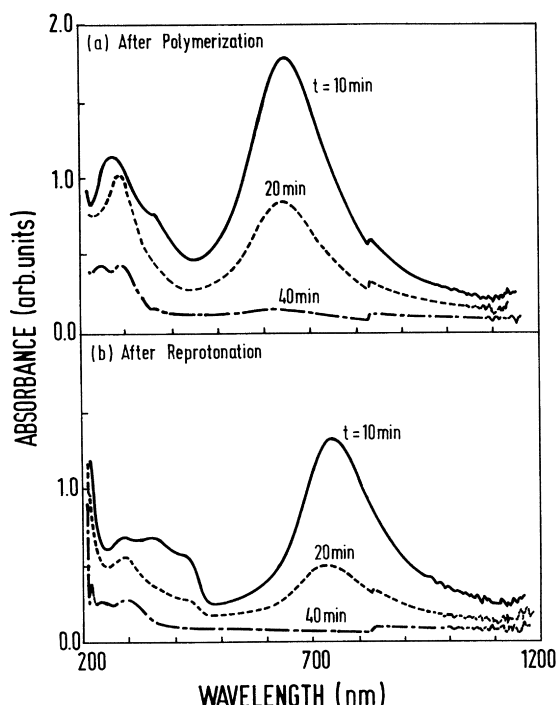
Fig. 2. UV–visible absorption spectra of (a) PANI–nylon 6 films after various polymerization times, and (b) the corresponding films after quenching with water and reprotonation with 2 M HCl.

region (which would indicate the dominance of intra-chain effects), indicates that the PANI salt formed comprises of short chains and the polarons are localized [13,14].

The spectra shown in Fig. 1 are for films synthesized using a polymerization time of 10 min. With an increase in polymerization time, the absorbance of the films decreases (Fig. 2). In addition, the 620 nm band in the spectrum of the film immediately after polymerization (Fig. 2(a)) and also the 750 nm band in the reprotonated film (Fig. 2(b)) show a blue shift with an increase in polymerization time. After 40 min of polymerization, the film is almost colorless with only a very slight tinge of violet. The data
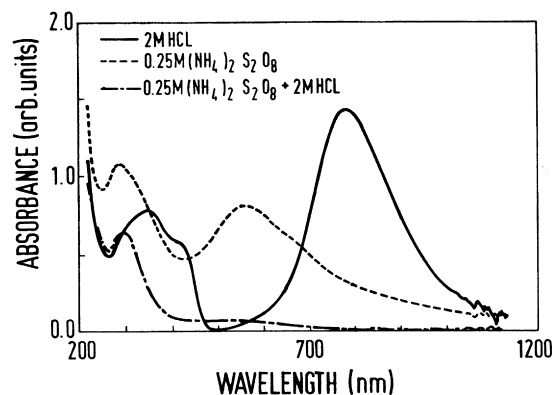

Fig. 3. UV–visible absorption spectra of film PA1 after soaking for 30 min in 2 M HCl; 0.25 M $(NH_4)_2S_2O_8$ in H_2O solution; and 0.25 M $(NH_4)_2S_2O_8$ in 2 M HCl.

shown in Fig. 2 is entirely different from those obtained with PANI composite films obtained by immersing aniline swollen polyethylene in $FeCl_3$ solution [6]. In the latter case, the transmission of the films shows a steady decrease with increase in polymerization time between 0.5 and 28 h. We attribute this difference to the differences in the thickness and type of the polymeric matrix used and the resultant effect on the diffusion behavior of the monomer and oxidant, as well as the oxidant used. The diffusion of aniline monomer and oxidant into the 15 μm nylon 6 matrix is more easily accomplished than in the polyethylene film of >40 μm. This can be substantiated by comparing the weight gained by the composite films (relative to the polymeric matrix's weight) in the two cases. In the present case, the weight gain after 10 min is 6.5% which then decreases with time, whereas for the PANI–polyethylene composite [6], the weight gain increases to about 10% after 200 min and remains constant thereafter.

We postulate that the results shown in Fig. 2 can be explained by the continual overoxidation of PANI as it is formed into either nigraniline (25% –NH–) or fully oxidized pernigraniline state while the films are immersed in the oxidant solution. PANI in these states existing in an acidic medium is prone to degradation by hydrolysis reactions resulting in shorter chains and soluble products such as p-benzoquinone [15–17]. Thus, the amount of PANI remaining in the film at any time is the net result of the polymerization and degradation reactions. The former is dominant at the initial stages, but the latter becomes more important as the monomer is consumed. To verify this postulate, two experiments were carried out. In the first experiment, a PANI–nylon 6 composite film obtained after 10 min of polymerization, 30 min of quenching with deionized water followed by 30 min of reprotonation with 2 M HCl (this film is denoted as PA1) is soaked either in 2 M HCl, 0.25 M $(NH_4)_2S_2O_8$ in water or 0.25 M $(NH_4)_2S_2O_8$ in 2 M HCl. The UV–visible absorption spectra obtained are shown in Fig. 3. It is obvious from this figure that there is no significant change if PA1 is soaked in 2 M HCl but within 30 min in 0.25 M $(NH_4)_2S_2O_8$ in 2 M HCl, the absorbance of the film is almost zero, similar to that observed in Fig. 2(b) for 40 min of polymerization time. The combination of oxidant and acid is significantly more effective than the oxidant in water in degrading the film, as can be seen by the results in Fig. 3.

In the second experiment, the effect of the quenching medium (0.5 M NaOH, water or 0.1 M HCl) on a PANI–nylon 6 composite film after 10 min of polymerization was investigated. The spectra obtained after the quenching and subsequent reprotonation steps are shown in Fig. 4(a) and (b), respectively. The spectra characteristic of neutral pernigraniline are evident when the quenching medium is either NaOH or water (Fig. 4(a)) and the absorbance is highest when NaOH is used as the quenching medium (Fig. 4(a) and (b)). Thus, NaOH being the most effective medium in quenching the polymerization reaction also preserves the
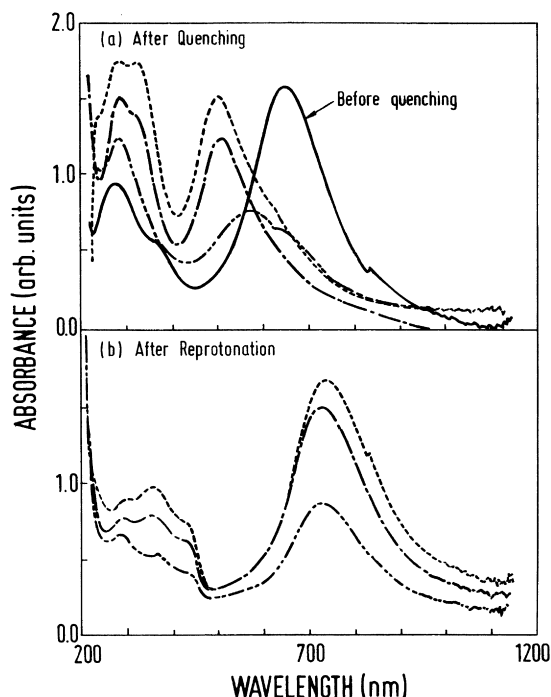
Fig. 4. UV–visible absorption spectra of PANI–nylon 6 films after 10 min of polymerization reaction and (a) quenched with different media: 0.5 NaOH (– –), H_2O (— - —), 0.1 M HCl (— - - —) for 30 min, and (b) the corresponding films from (a) after reprotonation with 2 M HCl for 30 min.
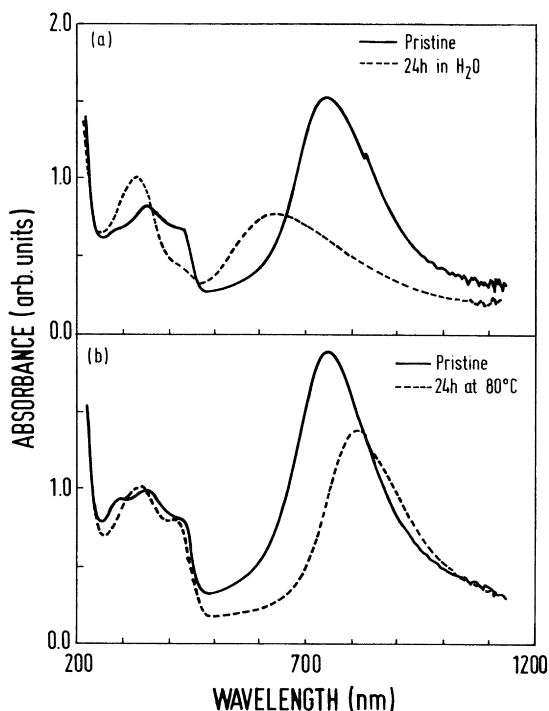

Fig. 5. UV–visible absorption spectra of (a) film PA1 before and after soaking for 24 h in water, and (b) film PA1 before and after 24 h at 80°C in air.
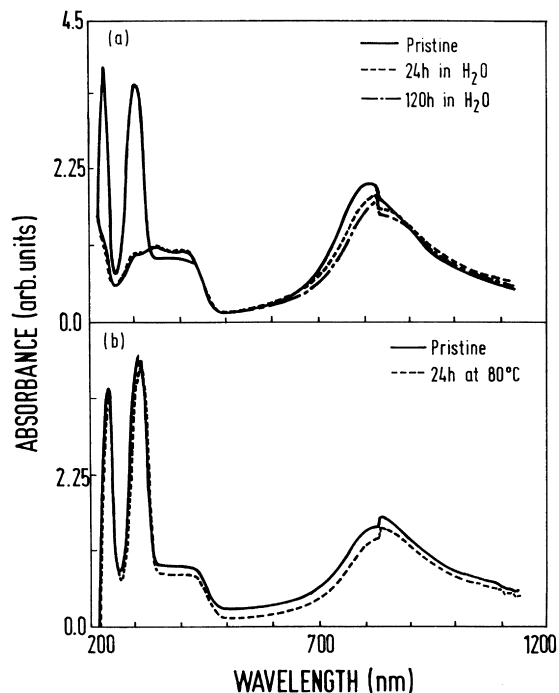

Fig. 6. UV–visible absorption spectra of (a) film PA2 before and after soaking in water for 24 h and 120 h, and (b) film PA2 before and after 24 h at 80°C in air.

PANI already formed. Conversely, if 0.1 M HCl is used as the quenching medium, the oxidation of the PANI continues in the film resulting in the least amount of PANI retained in the nylon 6 matrix (Fig. 4(b)). A comparison of Fig. 4(a) and (b) also shows that after the reprotonation step, an EM salt rather than protonated pernigraniline is obtained, regardless of the quenching medium. This corroborates the postulation that hydrolysis of pernigraniline in an acidic medium results in shorter chains of EM salt and soluble products [15].

The stability of the PANI–nylon 6 composite was tested using the film PA1. The UV–visible spectra of PA1 after 24 h in water and 24 h in air at 80°C are shown in Fig. 5(a) and (b), respectively. After 24 h in water, the spectrum obtained is that of EM base with the major absorption bands at 320 and 630 nm [13]. The Cl content in the film drops from 0.68 wt.% to almost nil, indicating that the Cl^- anions migrate out easily from the composite film and the EM salt is converted to EM base. Upon exposure of the PA1 film to 80°C for 24 h, the UV–visible spectrum retains the same shape albeit a lowering of the absorbance beyond 500 nm and a red shift of the 750 nm band to 830 nm are observed. Thus, PA1 retains the structure of EM salt and the observed effects are probably related to changes in the PANI chain conformation.

The stability of PANI–nylon 6 composite films in water can be greatly enhanced if the organic acids, sulfosalicylic acid (SSA) or polystyrene sulfonic acid (PSSA), are used instead of HCl in the preparation of the films. The films prepared in these manner are denoted as PA2 and PA3, respectively. The spectra of PA2 before and after 24 h and
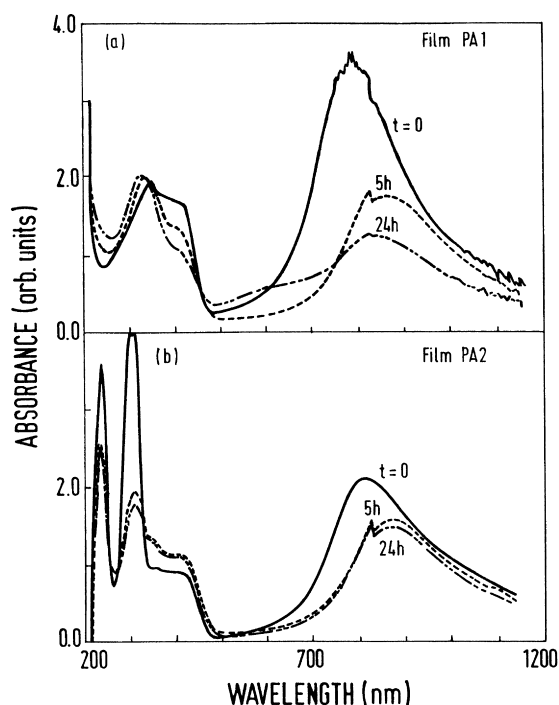
Fig. 7. UV–visible absorption spectra of (a) film PA1, and (b) film PA2, at various stages of the simulated weathering test.

120 h in water are shown in Fig. 6(a). There is a minimal change in the spectra beyond 350 nm even after 5 days in water. The most obvious change is the disappearance of the band in the 300 nm region after the first day. This band is associated with SSA and we have shown that when PANI is synthesized in SSA, an excess of SSA is retained in the polymer [18]. The "free" SSA anions are associated with H^+ rather than serving as counterions to the positively charged PANI chains, and are readily removed upon immersion in water. The SSA counterions, on the contrary, do not appear to migrate out of the polymer matrix. The S content decreases from 1.08 wt.% before water treatment to 0.56 wt.% after 24 h in water. Similarly for the PA3 film, the S content decreases from 1.39 to 0.73 wt.% and the spectra remain essentially unchanged after five days of treatment with water. Both the PA2 (Fig. 6(b)) and PA3 films do not show significant changes in their spectra upon heat treatment at 80°C for 24 h.

Table 1
Effect of weathering on the tensile strength of PANI–nylon 6 and PPY–nylon 6 composite films

Sample	Tensile strength (MPa)	
	Before weathering	After weathering (24 h)
PA1	120	100
PA2	110	97
PA3	130	110
PY1	81	74
PY2	80	75

The spectra of PA1 and PA2 after various stages of simulated weathering are compared in Fig. 7. The gradual conversion of the EM salt in film PA1 to the base form is evident from the decrease in the absorbance of the bands at 420 nm and in the 800 nm region and the increase in the absorbance at 630 nm after 24 h (Fig. 7(a)). In the case of film PA2, the most obvious change in the spectra is the decrease in the 300 nm band attributable to the loss of excess SSA, and after an initial red shift of the PANI salt spectra, there is no significant change after 5 h. The tensile strength of the PA1, PA2 and PA3 films range from 110 to 130 MPa before the weathering tests while the tensile strength of pristine nylon 6 is about 220 MPa. This decrease in tensile strength is caused by the partial destruction of the nylon 6 structure when the polymerization of PANI occurs in its matrix. After 24 h of weathering tests, the tensile strength of the PANI–nylon 6 composite films, PA1, PA2 and PA3, does not change by more than 20% (Table 1).

3.2. Polypyrrole–nylon 6 composites

The effect of polymerization time on the weight increase and tensile strength of PPY–nylon 6 composite films is shown in Fig. 8. Unlike the case of the PANI–nylon 6 films, the weight of the PPY–nylon 6 films increases with polymerization time and the weight increase after 4 h is doubled that obtained in 0.5 h. The tensile strength, in contrast, shows a dramatic decrease. The value after 4 h is only about 20% of the value after 0.5 h, indicating that extensive destruction of the crystalline structure of nylon 6 has occurred. In the absence of pyrrole, the tensile strength of nylon 6 after 4 h in $FeCl_3$ would decrease by less than 10%.

The UV–visible absorption spectrum of the film polymerized for 2 h in $FeCl_3$ (denoted as PY1) is shown in Fig. 9. The spectrum is characterized by a band at 480 nm and a high intensity tail extending into the near-IR region. The former was identified as a $\pi–\pi^*$ transition while the latter is characteristic of oxidized PPY as it is not observed in neutral PPY before exposure to O_2 [19]. The film after polymerization for 0.5 h gives an absorption spectrum showing the same features but at a lower absorbance, consistent with the smaller amount of PPY in the composite.

The stability tests were carried out with the PY1 film. This film has a surface Cl/N mole ratio of 0.25 (determined by XPS) and a bulk Cl/N mole ratio of 0.11 (determined by elemental analysis). The mole fraction of PPY in the PY1 composite film is estimated to be 0.16 from the C/N ratio of the composite film and the fact that the C/N ratio for pyrrole and nylon 6 is 4 and 6, respectively. Thus, the bulk Cl/N_{PPY} is estimated to be 0.63, which is much larger than the value of 0.25–0.33 expected for PPY doped by Cl^- anion [20–22]. From the XPS Cl2p core-level spectrum, it was determined that slightly less than half of the Cl exists as covalently bonded Cl ($Cl2p_{3/2}$ peak component at a binding energy of 200 eV) with remainder as Cl^- anions ($Cl2p_{3/2}$
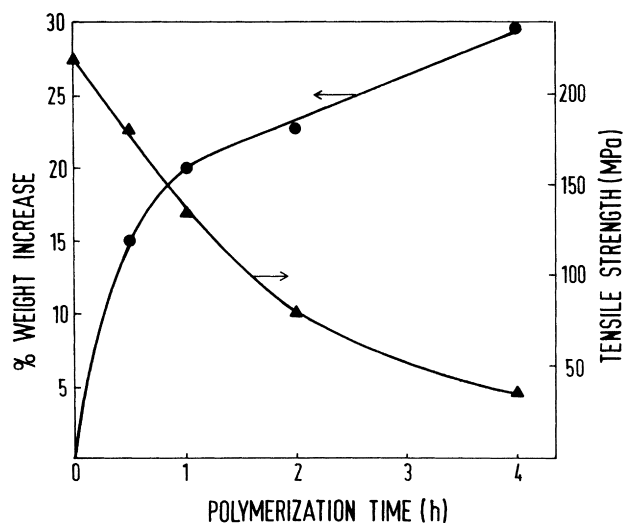
Fig. 8. Effect of polymerization time on the weight increase and tensile strength of PANI–nylon 6 composite films.

peak component at 197 eV) [23]. However, as XPS is a surface sensitive technique, the results from the XPS analysis may not be indicative of the situation in the bulk of the film. The iron content in PY1 is 1.4 wt.% and the Fe/N_{PPY} is estimated to be 0.18. The spectrum of PY1 after 24 h in water shows a slight blue shift of the $\pi-\pi^*$ transition absorption band (Fig. 9). The bulk Cl content has decreased by a factor of 3 as a result of the water treatment. The resistivity of the film also increases by a factor of 6 (from 1×10^4 Ω/sq), consistent with the loss of Cl^- anions from the film into the water. After 24 h at 80°C, the PY1 film turns opaque, and the absorbance exceeds the spectrometer's maximum value. This effect is likely to be caused by the iron chloride in the film reacting with air at elevated temperature to form iron oxide. The iron chloride may be in the form of the unreacted oxidant, $FeCl_3$, or $FeCl_2$ which is formed via the following polymerization reaction of pyrrole (assuming a doping level of 0.25):

$$n C_4H_5N + 2.25n FeCl_3 \rightarrow [(C_4H_3N) + Cl_{0.25}^-]_n + 2n HCl$$
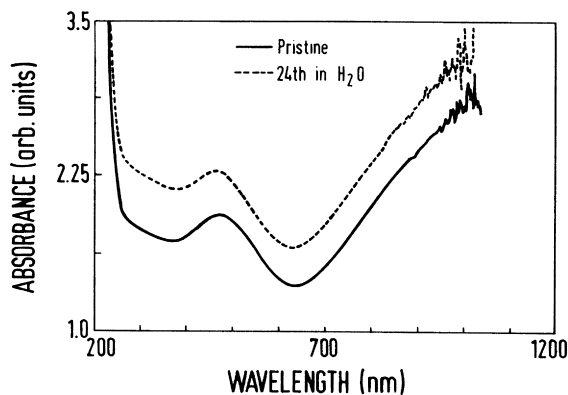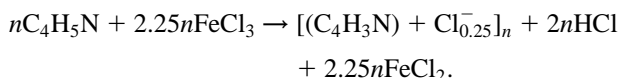
$$+ 2.25n FeCl_2.$$

Fig. 9. UV–visible absorption spectra of film PY1 before and after soaking in water for 24 h.
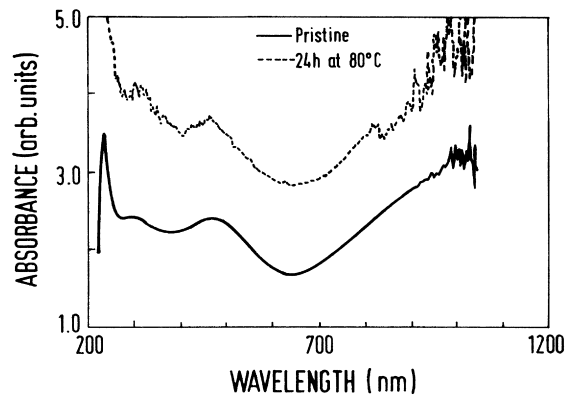

Fig. 10. UV–visible absorption spectra of film PY2 before and after 24 h at 80°C in air.

Since in some applications, it may be desirable to have transparent, conductive films, an attempt was made to reduce the iron content by soaking the PY1 film in water or in 0.5 M SSA for 24 h. The iron content after soaking in water and 0.5 M SSA for 24 h is 1.1% and 0.5%, respectively. The absorbance of the water soaked film subjected to 24 h at 80°C still exceeds the limit of the spectrometer. This increase in absorbance is much less for the SSA soaked film (denoted as PY2) as shown in Fig. 10. The resistivity of the PY2 film is 2 times that of the PY1 film. From elemental analysis (Table 2), the Cl/N and S/N mole ratios in PY2 are 0.021 and 0.020, respectively. The $(Cl^- + -SO_3^-)/N_{PPY}$ mole ratio is estimated to be 0.26, assuming no covalently bonded Cl. However, as some of the Cl is either covalently bonded to the PPY or associated with the remaining Fe, there may not be sufficient anions (Cl^- and $-SO_3^-$) to achieve a doping level of close to 0.3. This may partly explain the increase in the resistivity of the PY2 film over that of the PY1 film. However, the PY2 film is more stable in H_2O and after 24 h of immersion, there is no substantial increase in resistivity, unlike the PY1 film. As in the PANI–nylon 6 films, this is attributed to the greater ease of the Cl^- anions compared to the SSA anions to migrate out of the polymer matrix.

The spectra of PY1 and PY2 after 5 h of simulated weathering are compared in Fig. 11. The PY1 film gradually darkens under simulated weathering (Fig. 11(a)) and after

Table 2
Elemental analysis of PY1 and PY2 composite films

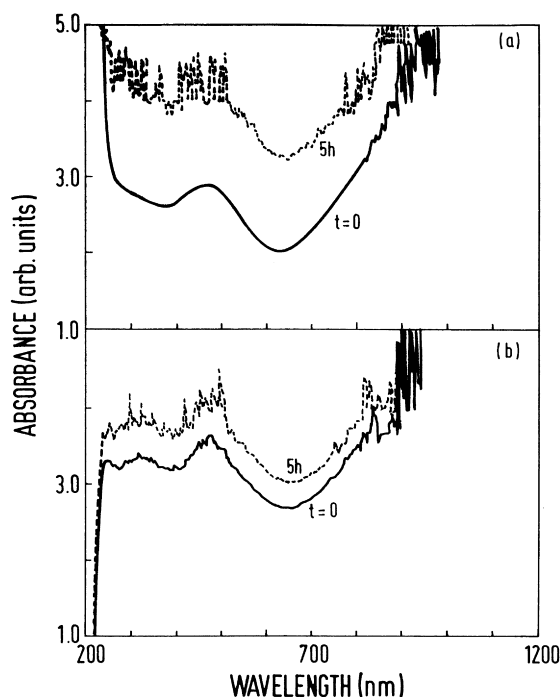| Element	PY1		PY2	
	wt.%	Mole ratio[a]	wt.%	Mole ratio[a]
C	59.2	5.7	60.8	5.8
H	10.1	11.7	8.76	9.9
N	12.1	1.0	12.3	1.0
Cl	3.3	0.11	0.66	0.021
S	—	—	0.55	0.020
Fe	1.4	0.028	0.50	0.010

[a] Normalized with respect to N.

Fig. 11. UV–visible absorption spectra of (a) film PY1, and (b) film PY2, before and after 5 h of simulated weathering test.

24 h the film is completely opaque and black. The PY2 film also darkens (Fig. 11(b)) but the increase in absorbance after 24 h of simulated weathering is less than that observed with PY1 after 5 h of similar treatment. This darkening effect is again attributed to the reactions of Fe remaining in the film. In this case, the reactions are accelerated by UV–visible irradiation rather than heat. From Fig. 11, it can be seen that the increase in absorbance is the most prominent change after weathering of the films and the other features of the spectra do not change substantially. However, after the weathering tests (24 h), both the PY1 and PY2 films show an increase in resistivity. The former by about a factor 4 and the latter by a factor of 2. The greater increase in resistivity of the PY1 film is again attributed to the migration of the Cl^- ions, as discussed before. Hence the resistivities of these films are similar after the test. Both films show only a marginal decrease ($< 10\%$) in tensile strength after the simulated weathering test (Table 1).

4. Conclusion

The synthesis of electroactive polymer–nylon 6 composite films can be easily achieved by immersing the monomer-containing nylon 6 films in an oxidant reaction. However, it was found that this diffusion–oxidation technique for the synthesis of the PANI composite films can easily cause the over-oxidation of PANI to soluble products

resulting in a decrease in yield with polymerization time. The Cl^- counterions to the PANI are easily removed when the film is immersed in water causing the PANI to revert to the base form. With SSA anions, the film can remain in the salt form after extended periods in water and under simulated weathering. In the case of PPY, the diffusion–oxidation technique can result in a much more substantial amount of electroactive polymer in the nylon 6 matrix. However, the tensile strength of the film decreases with a corresponding increase in PPY. With this technique, iron chloride is retained in the film and this results in blackening of the film at elevated temperature or under simulated weathering. The complete removal of the iron salt cannot be easily accomplished. SSA is more effective than water in reducing the iron content and the former also supplies counterions to replace the loss of Cl^- from the films. As a result, the treatment of the as-synthesized PPY–nylon 6 films with SSA results in a reduction of the blackening problems and an increase in stability in water.

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