Polymer 41 (2000) 1783–1790

polymer

Electroformation of conducting polymers in a hydrogel support matrix

B.C. Kim[a], G.M. Spinks[a], G.G. Wallace[a,*], R. John[b]

[a]Intelligent Polymer Research Institute, University of Wollongong Northfields Avenue, Wollongong, NSW 2522, Australia
[b]School of Applied Science, Griffith University, Gold Coast Campus, Parklands Drive, Southport, QLD 4217, Australia

Received 16 November 1998; received in revised form 6 April 1999; accepted 6 April 1999

Abstract

Conducting polymers have been electrochemically synthesised inside a hydrogel support matrix. The effect of electropolymerisation time on the electroactivity as well as the water content and dehydration/rehydration properties of the materials produced has been investigated.

Keywords: Conducting polymers; Hydrogel support matrix; Electropolymerisation

1. Introduction

Hydrogels and conducting polymers are two of the most promising types of polymers being used for new material development. Both hydrogels and conducting polymers are stimuli responsive materials whose dynamic characteristics are reasonably well understood. Hydrogels undergo phase transitions (volume changes) in response to changing environmental conditions such as temperature [1,2], pH [3], solvent composition [4], and electrical stimuli [5]. Conducting polymers also undergo chemical and physical changes in response to electrical stimuli. Ion exchange capacity [6], protein affinity [7], or enzyme bioactivity [8], tensile strength [9], conductivity [10] and optical properties [11–14], all change in response to the imposition of appropriate electrical potentials.

Despite the promising electrofunctional attributes of both classes of polymers there are several limitations that mitigate against their use in practical applications and/or devices. In the case of hydrogels electrical stimuli are not readily transmitted throughout the structure due to the low electronic conductivity of the supporting polymer network. Hence, the response times for anything other than microstructures are quite long. In the case of conducting polymers the ability to produce the materials in a wide range of geometries with different porosities and appropriate mechanical properties is limited. This is particularly true for insoluble conducting polymers prepared electrochemically and yet this method of formation is desirable if highly conductive, multifunctional polymers are to be produced.

As a result of these limitations, a number of workers have considered the use of different electrode substrates to modify the form of the conducting polymer produced electrochemically. For example, Martin and coworkers [15] have used porous electrodes to produce fibrillar materials. Growth within zeolite structures [16] has also been explored. Perhaps the most common hosts, however, are polymeric in nature. This is usually achieved by pre-coating the electrode with an insoluble polymer, such as polyvinylchloride [15], polyamide [16] or polyurethane [17]. The coated electrode is typically immersed in monomer solution and subsequent electropolymerisation of the monomer produces a conducting polymer composite material. Recently we have shown that electropolymerisation of conducting polymers is possible within a hydrogel matrix [18]. In the course of the present work the effect of monomer concentration and polymerisation time on the electroactivity, equilibrium water content, dehydration and rehydration behaviour of these conducting-polymer–hydrogel structures has been investigated.

2. Experimental

2.1. Materials

Acrylamide (AAm) was purchased from Sigma (USA), recrystallised from acetone and oven dried before use. N,N'-methylene-bis-acrylamide (MBA) and tetramethylethylenediamine (TEMED) were purchased from Aldrich Chemical Co. (USA) and were used for hydrogel preparation without further purification. Ammonium persulfate ($NH_4S_2O_4$) and

---

* Corresponding author.

PII: S0032-3861(99)00308-0

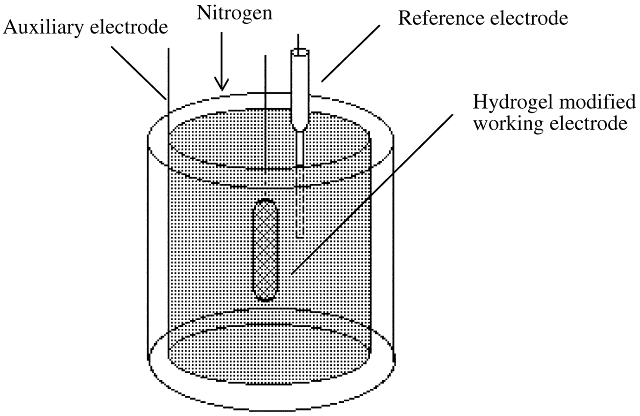


Fig. 1. Electrochemical cell used for synthesis and electrochemical polymerisation of the HCP blends.

sodium nitrate ($NaNO_3$) were purchased and used as received from Ajax (Australia). *p*-toluene sulfonic acid, sodium salt (PTS) was purchased from Merck (Germany) and used as received. Pyrrole (Merck) was purified by distillation prior to use.

2.2. Preparation of hydrogel encapsulated electrodes

Polyacrylamide gels were prepared as described elsewhere [19]. Briefly, 1.00 g of AAm monomer and 0.03 g MBA were added to 10 ml of deionised (Milli-Q) water. After purging with N_2 for 10 min, TEMED (60 μl) and ammonium persulfate (0.003 g) were added with vigorous stirring. Gelation typically occurred after 10 min at room temperature.

Hydrogel encapsulated electrodes were prepared by casting the gel solution around a 1.5 mm diameter polished (0.05 μm alumina) stainless steel wire. This was done by suspending the wire in the middle of a 5 mm diameter test tube approximately 5 mm from the bottom. The gel solution (as described in the previous paragraph) was then poured into the test tube and gelation allowed to occur. After gelation, the hydrogel encapsulated electrode was removed from the test tube and placed in a large beaker of Milli-Q water to extract any unreacted reactants. The water was replaced repeatedly over a period of two days.

2.3. Synthesis of hydrogel–conducting-polymer blends

Fig. 1 shows the electrochemical cell and electrode arrangement used for the synthesis of the hydrogel–conducting-polymer (HCP) blends. The hydrogel encapsulated stainless steel electrode was used as the working electrode in a conventional three electrode cell and placed inside a cylindrical platinum gauze auxiliary electrode. An Ag/AgCl reference electrode was positioned near the working electrode as indicated.

Aqueous pyrrole monomer solutions, of varying concentrations, were used for the electrosynthesis of conducting polymer (polypyrrole) throughout the hydrogel matrix. *p*-toluenesulfonate (sodium salt, 0.1 M) or 1 M $NaNO_3$ were used as supporting electrolytes for the electropolymerisation process. The hydrogel encapsulated electrodes were presoaked in the same solution to be used for electropolymerisation for 24 h. All pyrrole solutions were purged with nitrogen for 10 min to reduce O_2 levels and the electropolymerisation reactions were performed under a nitrogen headspace.

An EG and G Princeton Applied Research Model 363 Galvanostat/Potentiostat was used for galvanostatic and potentiostaic synthesis of the HCP blends. Applied current densities and potentials were as stated in the text and figures.

2.4. Electrochemical characterisation of the HCP blends

Electrochemical characterisation of the HCP blends was carried out using cyclic voltammetry (CV) in 1 M $NaNO_3$ solution. The electrochemical cell used was the same as that used for electrochemical synthesis (see Fig. 1). A BAS 100A electrochemical analyser was used to perform the CV experiments. Electrochemical parameters were as stated in the text and figures.

2.5. Conducting polymer content

The amount of conducting polymer (PPy) formed in the blends was determined gravimetrically. The pre-gel solution was poured into 10 pre-weighed cylindrical tubes prior to gelation. After gelation, samples were then dehydrated in fume hood at room temperature for 24 h and then moved to the oven at 60°C for 24 h. Finally the sample was dried to constant weight in the vacuum oven at 50°C for 3 days to determine the dehydrated weight (W_1). This weight (W_1) was found to be within 2% of the starting mass of AAm and MBA used. After electropolymerisation for 12 h the HCP blends were washed and dehydrated as described above and weighed. The average weight was obtained from the 10 samples (W_2). This process was repeated for three other electropolymerisation times (24, 48, 72 h).

The weight percentage of CP in the composite was calculated using Eq. (1):

$$\text{PPy content (\%)} = \frac{W_2 - W_1}{W_2} \times 100. \tag{1}$$

2.6. Equilibrium water content

The equilibrium water content (EWC) of polyacrylamide hydrogels and HCP blends were determined by measuring the weight difference between equilibrium hydrated and completely dried samples. Ten samples were cut from the swollen acrylamide gel, surfaces carefully wiped with a filter paper and the swollen weight determined (W_3). The EWC was the result of averaging the values from at least

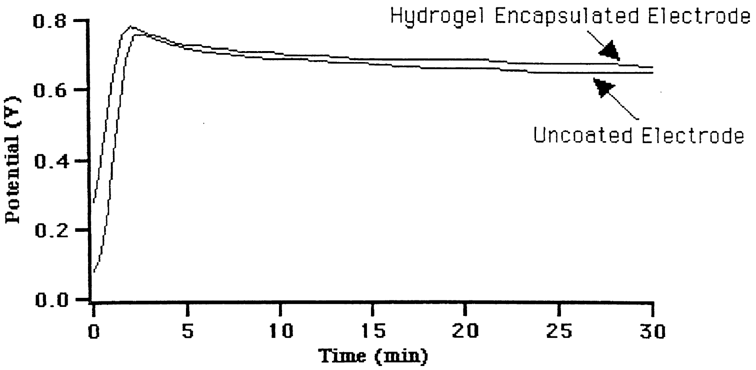


Fig. 2. Chronopotentiogram monitored during PPy growth on bare S.S working electrode and polyacrylamide hydrogel encapsulated SS working electrode. (Monomer concentration = 0.5 M, Supporting electrolyte = 1.0 M $NaNO_3$, Current density = 0.5 mA/cm^2).

three measurements (Eq. (2)):

$$\text{EWC (\%)} = \frac{W_3 - W_2}{W_3} \times 100. \qquad (2)$$

2.7. Dehydration and rehydration measurements

The gel-modified electrode and gel blends were immersed in a large amount of pure water for a week to remove residual chemicals. The swollen weight (W_3) of the fully hydrated samples were determined after carefully wiping off the surface water. These were allowed to dehydrate completely as described above. The weight of the samples during drying were measured at regular intervals (W_{Dt}) and the water content calculated using Eq. (3). The % dehydration was then plotted as a function of drying time:

$$\text{Water content (\%)} = \frac{W_{Dt} - W_2}{W_3} \times 100. \qquad (3)$$

Upon completion of the dehydration measurement, HCP blends were immersed in either Milli-Q water or 2.5% NaCl solution to observe rehydration behaviour and water uptake capacity. The weight of the samples during rehydration was measured at regular intervals (W_{Rt}). The water content during rehydration was obtained from Eq. (4). The final weight of rehydrated sample in different solutions was determined (W_4). Water uptake capacity was also calculated from Eq. (5). For pure acrylamide hydrogel, the same procedure was performed as described above. The final value reported is an average of the results from at least three measurements:

$$\text{Water content (\%)} = \frac{W_{Rt} - W_2}{W_{Rt}} \times 100 \qquad (4)$$

$$\text{Water uptake capacity (\%)} = \frac{W_4}{W_3} \times 100. \qquad (5)$$

3. Results and discussion

3.1. Synthesis of HCP blends

Fig. 2 shows the chronopotentiometric responses obtained for polypyrrole formation on a bare electrode and throughout the polyacrylamide hydrogel under galvanostatic conditions. Both responses are indicative of the formation of an electrically conducting phase on an electrode surface and are similar to conventional solution responses commonly observed in the literature for polypyrrole formation [20].

In both cases, the chronopotentiometric responses showed an initial sharp increase in potential (upon pyrrole oxidation) followed by a slow decrease in potential corresponding to subsequent oxidation/polymerisation. This decrease is indicative of growth of a conducting phase at the electrode surface. The final electropolymerisation potential was found to be approximately 30 mV higher for the HCP blend compared with the pure polypyrrole film. This was presumably due to the slightly more resistive environment inside the hydrogel structure compared with free electrolyte solution.

Fig. 3(a) shows the extent of PPy growth at various polymerisation times. Formation of the conducting polymer was initiated at the stainless steel electrode (as expected) and gradually expanded throughout the hydrogel structure with time. Visual inspection shows that as electropolymerisation time increases, the polypyrrole content also increased. For blends synthesised for longer than 2 h, the black polypyrrole phase had permeated throughout the entire hydrogel network. Despite this, gravimetric analysis indicated that the polypyrrole content was $< 5\%$ (w/w) of the total structure even up to electropolymerisation times of 24 h. The fact that the polypyrrole phase was able to penetrate the entire hydrogel network confirms that the polypyrrole phase was, in fact, electrically conducting (since new polymer formation will only be initiated electrochemically at a conducting surface).

HCP blends formed by electropolymerisation of polypyrrole for times longer than 10 h were found to have poor

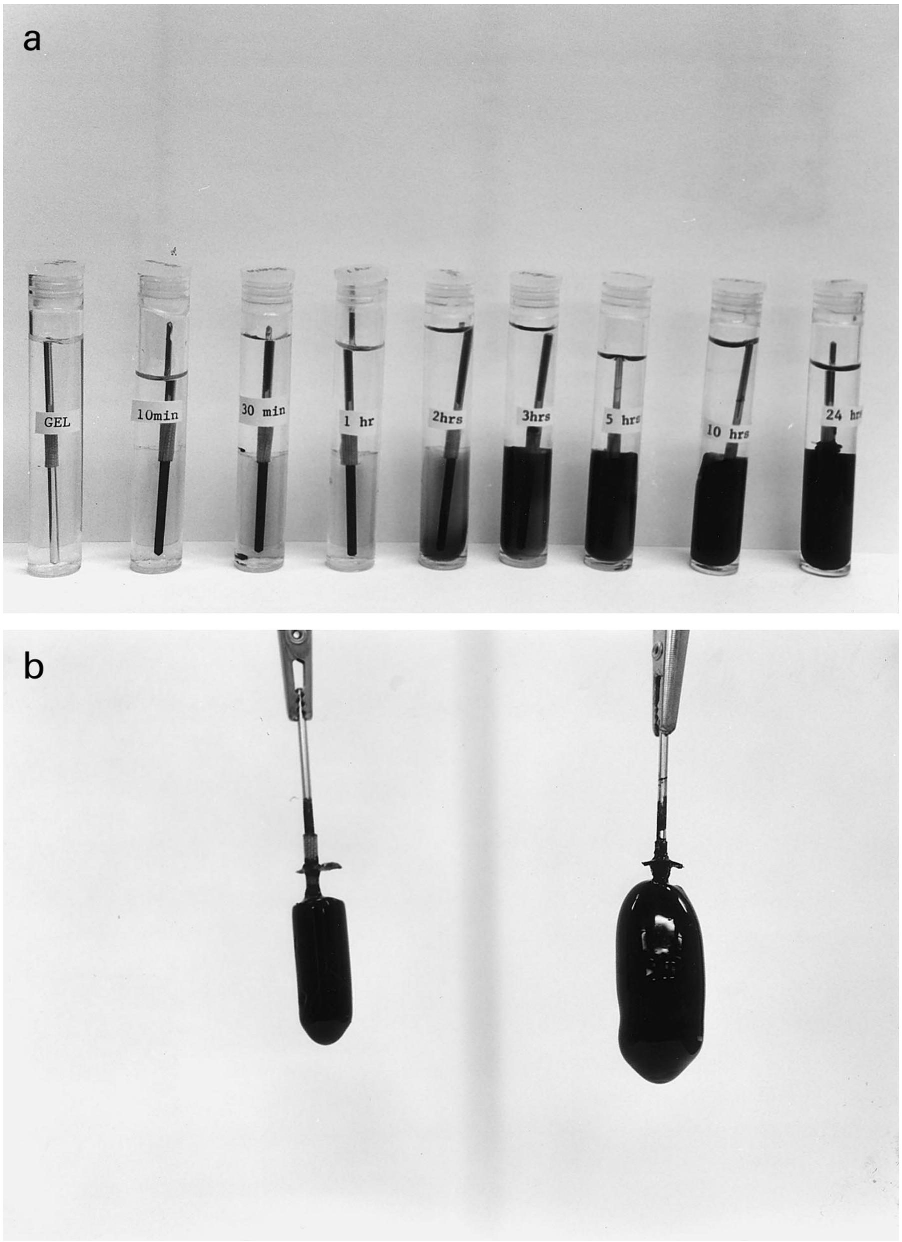
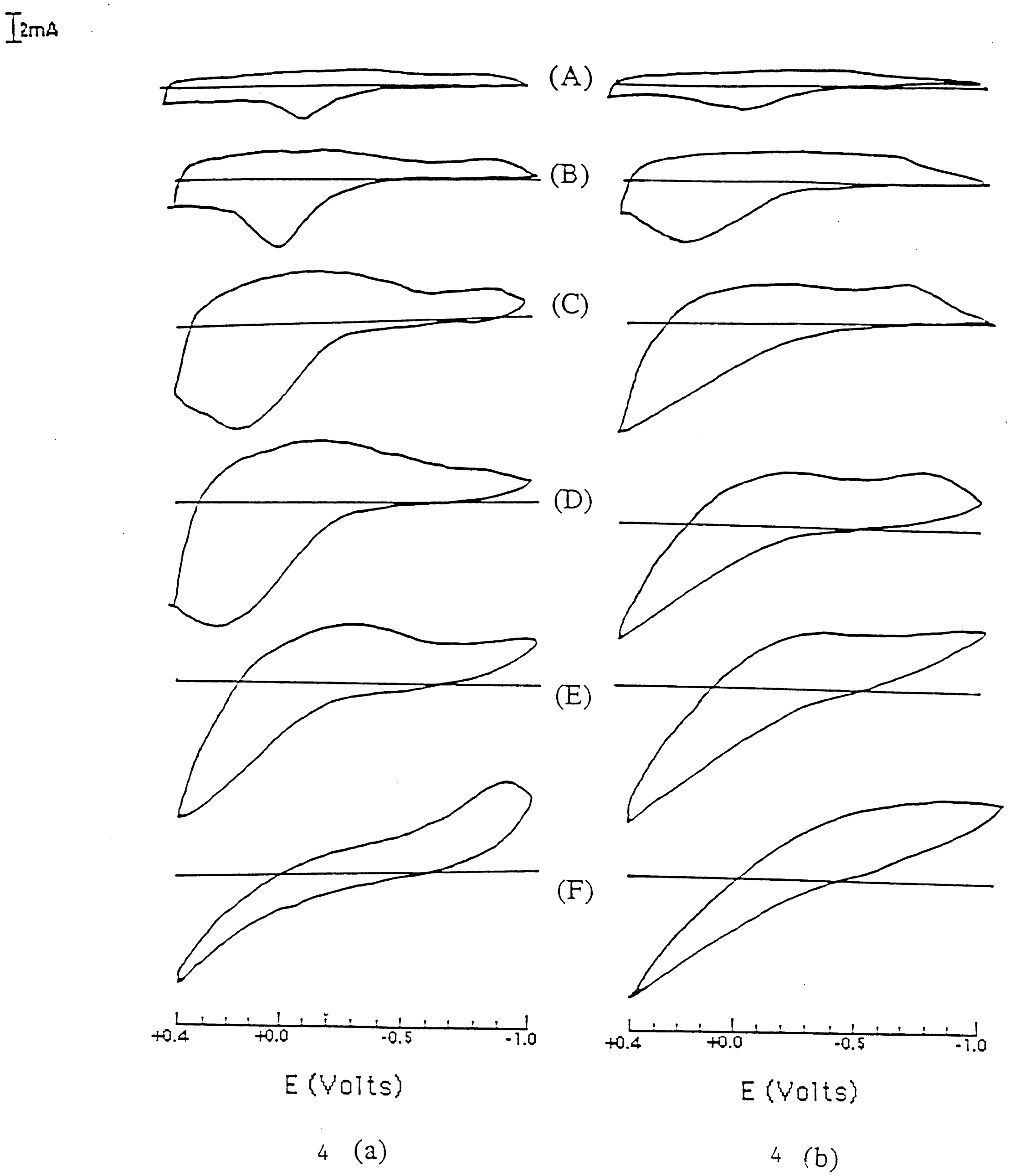


Fig. 3. (a) Polyacrylamide hydrogel and HCP blends prepared galvanostatically by varying electropolymerisation time and (b) HCP blends prepared galvanostatically for 10 h (left) and 24 h (right) of electropolymerisation in 0.5 M pyrrole monomer and 1.0 M $NaNO_3$ mixture solution (Current density = 0.5 mA/cm^2).

mechanical properties. Fig. 3(b) shows that ingress of water into these blends occurred to such an extent that the rigid hydrogel structure was completely compromised. This excessive ingress of water was due to increased osmotic effects due to the increase in polypyrrole (and associated counterion) content. As a result of the poor mechanical properties of these blends, we restricted further studies to blends synthesised for 10 h or less.

3.2. Electroactivity of HCP blends

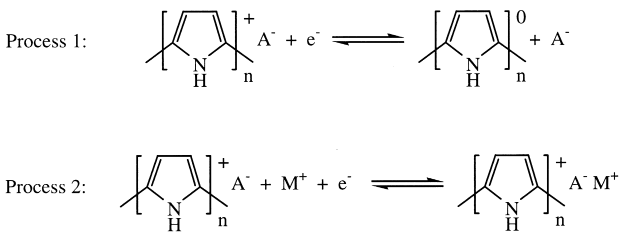
Cyclic voltammograms of the HCP composite show the characteristic redox responses commonly observed for conventional conducting polymer films at electrode surfaces. Fig. 4 shows a comparison between the cyclic voltammograms obtained for galvanostatically grown polypyrrole films (Fig. 4(a)) and HCP blends (Fig. 4(b)) at various polymer growth times. In both cases well defined polypyrrole redox behaviour is observed at shorter polymerisation times. At longer times, however, the cyclic voltammetric responses are less well defined with oxidation waves becoming more positive, reduction waves becoming more negative and a general “blurring” of the redox responses. Such behaviour is indicative of increased resistance and/or



4 (a)

4 (b)

Fig. 4. Cyclic voltammograms of (a) PPy and (b) HCP blends, grown galvanostactically for various electropolymerisation times. (A) 30 min; (B) 60 min; (C) 120 min; (D) 180 min; (E) 300 min; (F) 600 min. Scan rate: 5 mV s^{-1}, Supporting electrolyte: 1.0 M NaNO$_3$, Current density = 0.5 mA/cm^2.



Scheme 1.

Table 1
Equilibrium water content of PAAm hydrogel and PAAm hydrogel/PPy blends with different electropolymerisation time

Time (h)[a]	EWC (%)
0	91
1	91
2	90
3	91
5	91
7	91
10	90

[a] Electropolymerisation time to produce conducting polymer.

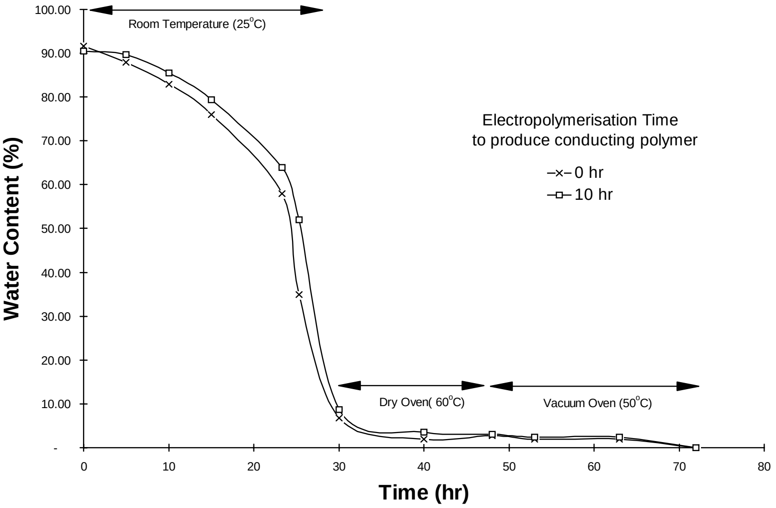


Fig. 5. Dehydration of hydrogel and hydrogel/polypyrrole blends with different drying condition. Drying conditions: ambient air (0–24 h); fume food at 60°C (24–48 h); vacuum oven at 50°C (48–72 h).

sluggish electron/ion transfer as the conducting polymer phase increases in thickness. This is not surprising given the electrochemical redox switching properties of polypyrrole. Scheme 1 shows that polypyrrole oxidation/reduction must be accompanied by concomitant ion transport to maintain electrical neutrality within the polypyrrole structure. If ion movement is slow (as is the case with thick films) then redox switching will also be slow. Such behaviour is reflected in the cyclic voltammetric responses of both Fig. 4(a) and (b) at longer polypyrrole deposition times.

Closer comparison of Fig. 4(a) and (b) shows that the loss of well defined redox behaviour occurs at shorter growth times for the HCP blends compared with the conventional films. Ion transport in and out of the entire HCP blend would be expected to be significantly more difficult than for the compact films and this is reflected in the cyclic voltammograms obtained.

Some of the original redox switching features of the CV response are regained by increasing the upper potential limit to $+1.00$ V. The positive shift in the polypyrrole oxidation potential up to approximately $+0.60$ V is an indication of the slower ion movement and/or the more resistive nature of the conducting polymer in the hydrogel network.

A final point worth noting regarding the redox properties of the HCP blends concerns the two processes outlined in Scheme 1. We have shown in previous studies [21] that for simple anions (A^-), such as NO_3^- and Cl^-, process 1 (i.e. anion transport) will predominate for relatively thin, porous polypyrrole films. Conversely, for relatively thick, non-porous films process 2 (i.e. cation transport) will be predominant. One of the distinguishing features of cation insertion during electrochemical reduction is the appearance of a separate reduction wave [21] in the region -0.6 to -1.0 V (vs Ag/AgCl). Fig. 4 shows that despite the porous structure

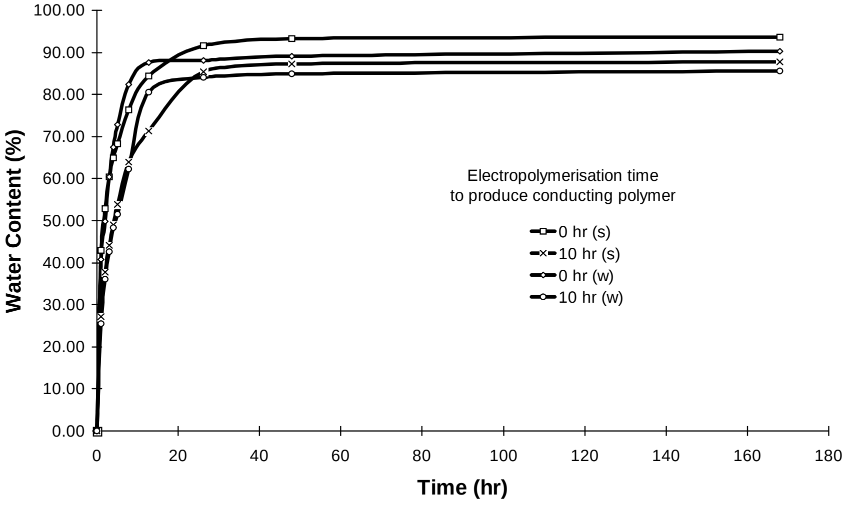


Fig. 6. Rehydration of hydrogel/polypyrrole blends in different solution; water (w) and 2.5% NaCl solution (s).

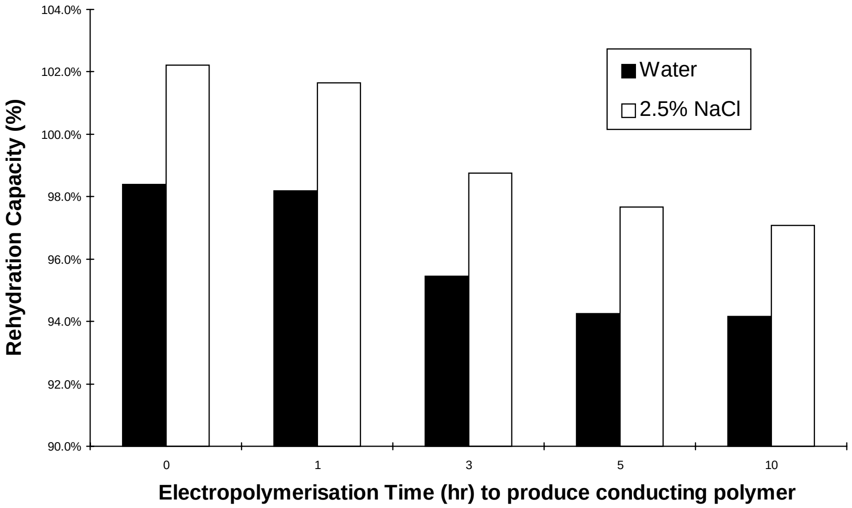


Fig. 7. Rehydration capacity of hydrogel and hydrogel/polypyrrole blends in different solutions: water and 2.5% NaCl.

of the HCP composite there is evidence of cation exchange processes occurring. This indicates that anion transport alone is insufficient (at longer polymer growth times) to accommodate the redox switching of the polypyrrole phase when larger amounts of polypyrrole are present.

3.3. EWC of HCP blends

Equilibrium water content measurements were carried out as described in the experimental section. The effect of electropolymerisation time on water content of the HCP blend is depicted in Table 1. The results show that the incorporation of PPy into the hydrogel has no significant effect on the water content of the fully swollen hydrogel. This reflects the relatively small amount of PPy ($< 5\%$ of the fully hydrated material) that is incorporated into the blends.

3.4. Dehydration and rehydration behaviour

HCP blends were dried under different conditions and the rates of dehydration of the blends are shown in Fig. 5. The initial dehydration rate for pure AAm hydrogel was slightly higher compared to the blends. For the HCP blends there may be retardation in the diffusion of water through the three-dimensional network due to the presence of PPy formed in the porous hydrogel network.

Rehydration tests were carried out in two solutions: Milli-Q water and 2.5% NaCl solution. The degree of rehydration in each solution for the different blends are summarised in Fig. 6. The rate of rehydration is markedly different for the different blends. Samples prepared using longer electropolymerisation times were slower to rehydrate. This presumably reflects the less hydrophilic nature with PPy present in the hydrogel network.

The final water capacity of the blends was determined in the two rehydration solutions (Fig. 7). The maximum water content decreased with increasing PPy content for blends prepared up to 10 h polymerisation time. This implies that PPy in the blends affects the water affinity after a dehydration/rehydration cycle. The reason for this change is not yet known. In all cases the water content was higher when the hydrogel was rehydrated in salt water.

4. Conclusions

It has been found that PPy can be incorporated electrochemically into the acrylamide hydrogel network. The polyacrylamide hydrogel/PPy blends are redox active and exhibit conductive properties. However, the kinetics of the redox switching processes are retarded in the hydrogel-conducting polymer materials due to reduced ion mobility and/or decreased electronic conductivity within the blends.

Addition of conducting polymer into the gel network had little effect on the water content. The EWC of the blends is very similar to the hydrogel alone. However, dehydration and rehydration rates were slightly slower when higher amounts of PPy were added to the gel.

Acknowledgements

The authors are grateful for the continued support of the Australian Research Council and to the support of MM Cables via an ARC SPIRT Grant.

References

[1] Aoki T, Kawashima M, Katono H, Sanui K, Ogata N, Okano T, Sakurai Y. Macromolecules 1994;27(4):947–952.
[2] Sasase H, Aoki T, Katono H, Sanui K, Ogata N. Makromol Chem Rapid Commun 1992;13:577–581.
[3] Hu Y, Horie K, Tori T, Ushiki H, Tang X. J Polym 1993;25(2):123–130.
[4] Hirokawa Y, Tanaka T. J Chem Phys 1984;81:6379.

[5] Tanaka T, Nishio I, Sung ST, Ueno-Nishio S. Science 1982;218:467.
[6] Ge H, Wallace GG. React Polym 1992;18:133.
[7] Hodgson AJ, Lewis TW, Maxwell KM, Spencer MJ, Wallace GG. J Liq Chromatogr 1990;13:3091.
[8] Lu W, Zhou D, Wallace GG. Anal Commun 1999; in press.
[9] Burford RP, Murray P, Spinks GM, Wallace GG. Synth Met 1999; in press.
[10] John R, Wallace GG. J Electroanal Chem 1993;354:154.
[11] Sapp SA, Sotzing GA, Reddinger JL, Reynolds JR. Adv Mater 1996;8:808.
[12] Sotzing GA, Reynolds JR, Steel PJ. Chem Mater 1996;8:882.
[13] Hyodo K. Electrochim Acta 1994;39:265.
[14] Chandrasekhar P, Masulautis AM, Gumbs RW. Synth Met 1990;36:303.
[15] Niwa O, Kikita M, Tamamura T. Makromol Chem Rapid Commun 1985;6(6):375–379.
[16] Selampinar F, Akbulut U, Yalcin T, Suzer S, Toppare L. Synth Met 1994;62:201–204.
[17] Ruckenstein E, Chen JH. Polymer 1990;32(7):1230–1235.
[18] Small CJ, Too CO, Wallace GG. Polym Gels Networks 1997;5:251–265.
[19] Hu DSG, Lin MTS. Polymer 1994;35(20):4416.
[20] Selaneek WR, Erlandsson R, Prejza I, Lundstrom I, Inganar O. Synth Met 1983;5:125.
[21] John R, Wallace GG. J Electroanal Chem 1993;354:145.