Composites of Conducting Polymers: Polyacetylene–Polypyrrole

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Electropolymerization of pyrrole onto polyacetylene (pac) gives conducting composites the morphology of which depends on the initial doping state of the pac.

The amount of work on conducting polymers has been increasing for several years. Most studies have focused on the pure polymers, polyacetylene (pac) and polypyrrole (ppl),[1] although composites with pac as one of the components have been described.[2] In all of these composites, however, pac is the only conducting component.

The high porosity and surface area of pac films has created interest in their use as electrode materials,[3] but the air-sensitivity of pac is a major shortcoming.[4] Ppl, on the other hand, has the greatest air stability of all the conducting polymers tested so far, but its surface area is relatively small and its mechanical properties, as a freestanding film, are not very good.[5]

We report here the novel combination of pac and ppl to form composites which exhibit properties of both polymers. The composites were formed by electropolymerization of pyrrole onto a pac film used as the anode, under conditions that are usual for ppl syntheses.[6] Depending on the initial doped state of the pac film, composites with different morphologies were synthesized.

Using undoped pac films the resulting composites [type (A)] have a sandwich-like structure. Tight layers of ppl are polymerised on the surface of the pac film as revealed by scanning electron microscopy (S.E.M.) (Figure 1). If the starting pac films were doped (*e.g.* with $InCl_4^-$, $FeCl_4^-$ or electrochemically with ClO_4^-, BF_4^-) before pyrrole was added to the electrolyte solution, the composites formed [type (B)] had the same porous morphology as the original pac film. No distinct ppl layer could be detected at up to 40 000 times magnification.

During the electrolyses an area of red colour developed in the electrolyte solutions close to the pac anode probably due

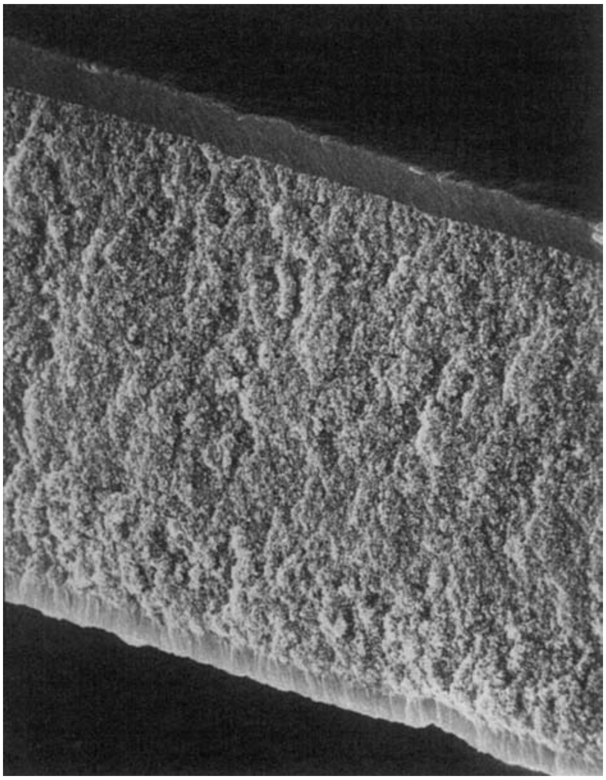

Figure 1. Cross section (× 1000) S.E.M. microphotograph of a type (A) pac–ppl composite.

to the formation of pyrrole oligomers.[7] Interestingly, this colour was not detected in polymerizations using platinum anodes.

The progress of the polymerization of the pyrrole could be readily monitored by observing the dull black layer of ppl forming on the shiny pac surface. For the undoped pac films the polymerization started at the contact to the current supporting wire (after a short induction period) as indicated by a red area in the solution. From this region the polymerization of pyrrole proceeded slowly along the film (almost identically on both of its sides). For the doped films, the polymerization started over the whole surface of the film immediately after application of the voltage. In fact, the red colour developed as soon as the doped pac came into contact with the electrolyte–pyrrole solution, *i.e.*, without an applied voltage. The electrical conductivity of both kinds of composite is *ca.* 20—40 Ω^{-1} cm^{-1} and they show excellent air and water stability† compared to doped pac (see Figure 2 and 3).

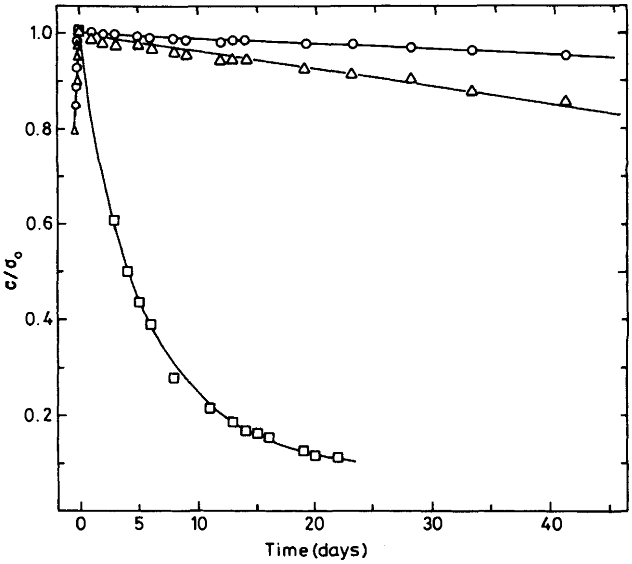

Figure 2. Relative electrical conductivity (σ/σ_0) *vs.* time (days) of exposure to air (*ca.* 40% relative humidity, ref. 8) of the conducting polymer films. △: composite type (A) (σ_0 = 38 Ω^{-1} cm^{-1}); ○: composite type (B) (σ_0 = 32 Ω^{-1} cm^{-1}); □: $InCl_4^-$ doped pac [σ_0 = 80 Ω^{-1} cm^{-1}, dopant concentration (d.c.) = 2.2%]. When exposed to air the composites first show an increase in conductivity as observed for ppl. Their conductivity is therefore scaled against the maximum conductivity taken as σ_0.

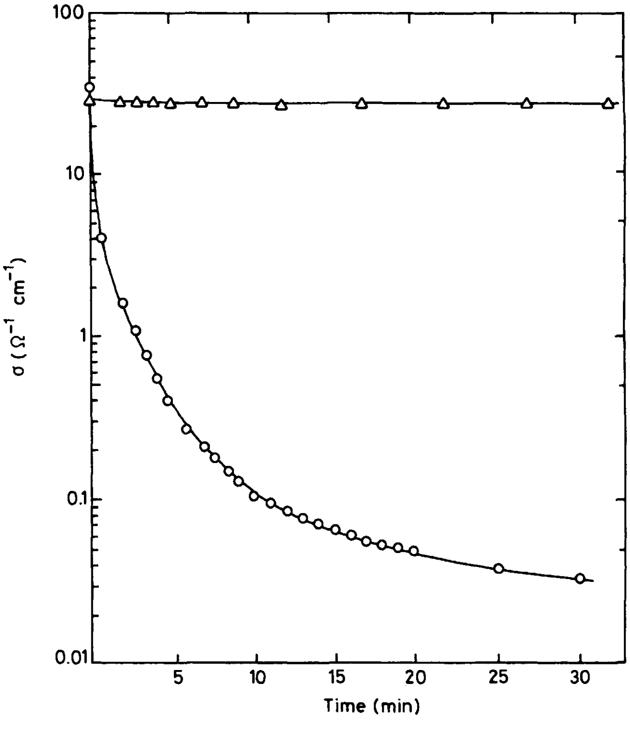

Figure 3. Electrical conductivity σ (Ω^{-1} cm^{-1}) *vs.* time (min) of insertion into water. △: type (B) composite; ○: $InCl_4^-$ doped pac (d.c. = 4.3%). The samples were exposed to air prior to insertion into water.

Further support for the proposed structures of the composites was provided by compensation studies with ammonia. Moreover, these indicated that both components support the current in the composite. Doped pac is much more sensitive to ammonia than ppl.‡ For both composites (A) and (B) the conductivity along and through the film was measured before and after 3 h exposure to the vapour above a concentrated ammonia solution. For composite (B) the conductivity in both directions was diminished by a factor of 30 whereas for composite (A) that along the film decreased by a factor of 17 while the conductivity through the film was 4600 times smaller. From these values and from the S.E.M. microphoto-

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† In fact, polymerization of pyrrole and washing of the resulting films with acetonitrile (4 times) can be done in air without deterioration of the resulting composite.

‡ For $FeCl_3$-doped pac the conductivity is diminished by a factor of > 10^6 on 20 min exposure to ammonia vapour. For ppl this diminishing factor is only ten (ref. 9).

graphs we deduce that in composite (B) each individual pac fibril is covered with a thin ppl layer throughout the whole of the pac film, whereas in composite (A) ppl formed only on the outside surface of the pac film.

The mechanical properties of the composite films have not been examined yet, but from our experience in handling them we can say that they resemble those of doped pac films. The ppl layer in composite (A) films does not peel off, even on scratching.

The e.s.r. spectra of composites (A) and (B) are apparently identical and consist only of a single very intense and narrow, symmetrical signal§ ($g = 2.0027$; $\Delta H^{\mathrm{pp}} = 0.2$—$0.3$ G¶) similar to that reported for ppl.[9]

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§ For the $FeCl_3$-doped samples, the signal is superimposed upon the broad (ΔH^{pp} *ca.* 400 G) Fe^{3+} signal.

¶ 1 G = 10^{-4} T.

References

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