Conductive Composites from Poly(vinyl chloride) and Polypyrrole

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The electrochemical polymerization of pyrrole on a platinum electrode covered with a film of poly(vinyl chloride) produces a dark brown, ductile, and flexible composite polymer film with an electrical conductivity comparable to polypyrrole, and mechanical properties very similar to poly(vinyl chloride).

In the last few years, there has been increasing interest in semi-conducting polymer films. Most of the work in this area has been concentrated in two main classes of polymers: polyacetylene and its derivatives[1] and polyheterocyclic cations.[2] The interest in polyacetylenes stems from their good mechanical properties which are associated with high electrical conductivity (σ) when doped with iodine (σ = *ca.* $10^3\ \Omega^{-1}$ cm^{-1}).[3] On the other hand, polyheterocyclic cations such as polypyrrole exhibit high electrical conductivity (σ = *ca.* $100\ \Omega^{-1}$ cm^{-1}) associated with high stability when exposed to ambient conditions.[4] The drawbacks of these polymers are, for polyacetylene, its poor stability at ambient conditions,[5] and for polypyrrole, its poor mechanical properties as indicated by its low elongation at break and its brittleness.[6] These properties severely restrict the technological application of these two classes of polymers.

It has previously been demonstrated that polymer composites can be produced by the sorption of a liquid or gaseous monomer in a host polymer followed by irradiation with u.v. light. In this case, the polymerization of the second monomer was shown to occur in the bulk of the host polymer matrix, thereby allowing the composite to retain primarily the properties of the host polymer.[7] Poly(vinyl chloride) (PVC) is one of the most versatile materials produced by the polymer industry. It is used in many applications, either in the pure form, plasticized, or in blends. Its mechanical properties can be varied simply by blending it with another polymer such as poly(vinyl alcohol), or by the addition of a plasticizer.

In this communication, we present an electrochemical method for producing flexible, free-standing composite polymer films from PVC and polypyrrole (PPY). These films have good electrical conductivity similar to pure PPY films (σ = *ca.* $50\ \Omega^{-1}$ cm^{-1} at room temperature), yet they retain the favourable mechanical properties of the host PVC film.

Composite films of PVC/PPY were prepared by constant potential electro-oxidation at +1.15 V, *vs.* Na saturated calomel electrode, using a platinum electrode already coated with PVC film (4—17 μm thick). The PVC film was coated on the electrode surface from a 10 g/l tetrahydrofuran solution, using low molecular weight, commercially unstabilized PVC. The composite films were prepared in a three-electrode, single compartment cell containing 0.006 M pyrrole in 0.1 M tetraethylammonium fluoroborate (TEAFB)–acetonitrile (dry) solution.

Minutes after the electropolymerization reaction is begun, the current–time plot achieves steady state, and the PVC film begins to darken, indicating the growth of PPY within the PVC (10 μm thick) matrix. When the PPY film is grown for 45 to 120 min, the PPY film grows beyond the thickness of the PVC film. In this instance, both faces (*i.e.*, the side that faces the electrode prior to being peeled off, and the side that faces the solution) of the free-standing composite film are electrically conducting. When the PPY growth time is less than 30 min, for example at 15 min, the limited time does not allow the thickness of the PPY film to reach that of its host. Thus, only the face which was attached to the electrode is electrically conducting. However, in order to obtain a film that is electrically conducting on both faces, it is not necessary to grow a thick layer of PPY on the face of the PVC film. Composites grown for slightly over 30 min produce such a film.

The electrical resistance of the free-standing films was measured utilizing a four-probe device, and the film thicknesses were measured *via* an alpha-step apparatus. The electrical conductivity of the composite films ranges from 5 to 50 Ω^{-1} cm^{-1}, similar to the highly conducting pure PPY films. The composite films show negligible change in their electrical conductivity even after 30 days of exposure to ambient conditions.

The rate of electropolymerization must depend on the diffusion of pyrrole across the PVC film to the electrode surface,[8] suggesting that the PVC film is highly permeable. This is not surprising, since the solubility parameter values are similar for PVC and acetonitrile.[9] Thus, acetonitrile is expected to swell the PVC and expose the Pt surface. The permeability of the PVC film was estimated using the ferrocene–ferrocenium reversible couple. The voltammogram of this couple shows the usual redox peaks even though they are *ca.* 20 times smaller in peak height. The peak heights also exhibit a small dependence on sweep rate (v). The peak current–sweep rate plot (i_p *vs.* $\sqrt{v}$) yields a diffusion constant (D) of 3×10^{-8} cm^2 s^{-1}, and a D/δ of 10^{-4} cm s^{-1} (δ = film thickness). This value is intermediate between the value for solution and for a highly cross-linked polymer film.

The transmission infrared spectrum (i.r.) of the PVC/PPY composite film reveals a superposition of the individual i.r. spectra of the parent polymers. The characteristic bands occur at 1550 (PPY) and 1440 cm^{-1} (PVC).

The mechanical properties were measured by the stress–strain technique using a Model 1122 Instron apparatus. The mechanical properties of the composite film, and those of pure PPY and PVC are summarized in Table 1. All of the films were subjected to the same conditions, even the pure PVC film on Pt was electro-oxidized for 1 h, in the absence of pyrrole. Comparison of the data reveals that both percent elongation at break and percent elongation at yield can be dramatically improved for pure PPY by incorporating it into a host polymer, *i.e.* , the PVC/PPY composite. The percent elongation of PVC can be further improved by the addition of a plasticizer. Thus, the composite film incorporates the advantageous mechanical properties of its host, while retaining the high electrical conductivity of pure PPY.

Table 1. Tensile strength (σ_b), percent elongation at break (ε_b), percent elongation at yield (ε_y), and conductivity (σ) for the materials discussed in this communication.

Material	σ_b (N mm^{-2})	ε_b	ε_y	σ (Ω^{-1} cm^{-1})
PVC	10	21	4	—
PPY[a]	44	5	—	30—60
PVC/PPY	12	22	6	5—50

[a] Ref. 6.

In conclusion, poly(vinyl chloride)/polypyrrole composite films can be prepared by standard electrochemical methods,[10] producing a conductive plastic with improved mechanical properties and stability to ambient conditions. These properties should make this composite very attractive for a wide range of technological applications.

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10 Similar work has been carried out by G. B. Street of this laboratory using poly(vinyl alcohol) as the matrix resin. G. B. Street, personal communication.