

Conductive Composites prepared by Electrochemically Polymerizing Pyrrole in Poly(Vinyl Chloride) blended with an Electrolyte

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Electrochemically prepared composites of poly(vinyl chloride) and polypyrrole significantly improve their uniformity in electrical conductivity and their resistance to mechanical delamination when a certain amount of electrolyte is mixed with poly(vinyl chloride) prior to the electrochemical reaction.

In recent publications,^{1,2} it has been reported that conductive polymer composites can be prepared by electrochemically polymerizing pyrrole on a working electrode coated with a polymer such as poly(vinyl chloride), PVC. Samples prepared by this method have shown a conductivity as high as 50 S cm^{-1} . A cursory study by us has shown, however, that the conductivity along the film surface direction is highly nonuniform across the thickness, being most conductive near the electrode side and least so at the free surface adjacent to the solvent. Furthermore, the nonuniformity persists even after a conductive polypyrrole layer begins to form and grow at the free surface of the film. The growth of the conductive network within the PVC film requires the presence in the film of a sufficient concentration of electrolyte; however, the maximum amount of electrolyte that can diffuse into the film with the solvent is very low, being *ca.* 0.6 wt%. In this communication, we demonstrate that the uniformity of conductivity can be improved significantly if we blend PVC with the electrolyte before the polymer is coated onto the electrode for the electrochemical treatment.

Unplasticized PVC, supplied by the B. F. Goodrich Co., was used as the host polymer. The polymer was dissolved in

tetrahydrofuran, THF, at a ratio of 10 g per 0.1 l. This solution was then applied on a working electrode made of an indium-tin oxide (ITO) coated soda-lime glass plate ($0.1 \times 2.5 \times 7.5 \text{ cm}^3$) by a vertical dip coating method. Typically, the dried PVC film had a thickness of *ca.* $1.8 \mu\text{m}$ and covered an electrode area of *ca.* $2.5 \times 5 \text{ cm}^2$. Films of the PVC-electrolyte blend were prepared in the same manner using a solution of PVC-THF-electrolyte-MeCN in the ratio of 10 g-0.1 l-0.5 g-0.01 l. The electrolyte material was tetraethylammonium tetrafluoroborate, TEAFB, supplied by the Aldrich Chemical Company.

The conductive composite was prepared using a two-electrode arrangement in a single compartment cell which contains 0.2 M of TEAFB and 0.1 M of pyrrole in distilled MeCN. With a platinum plate ($0.2 \times 4 \times 10 \text{ cm}^3$) as the counter electrode, a constant voltage of 2 V was applied between the two electrodes placed 1 cm apart.

Conductivity measurements along the film surface direction, σ_{\parallel} , were performed using a four probe technique. Values of σ_{\parallel} at the film surface on the electrode side (ITO) were measured after the film was peeled off from the substrate. For measurements of conductivity across the film thickness, σ_{\perp} ,

the free surface of the film was electroded with *ca.* 60 nm-thick gold by vapour deposition over an area of *ca.* 0.2×0.5 cm². All conductivity measurements were carried out in vacuum at room temperature. Film thicknesses were measured either optically by the Nomarsky technique or with a dial gauge having a sensitivity of 0.5 μ m.

During the experiment the thickness of the polymer film increased substantially after a few minutes of electrochemical treatment. This increase may be attributed to a combination of two factors, namely, (i) swelling due to penetration of the film by both the pyrrole monomer and the electrolyte which dominates in the first 20 min of reaction and (ii) formation and growth of a pure polypyrrole (PPY) layer outside the film which becomes increasingly more pronounced as the reaction time t_p exceeds 20 min. Evidence of growth of PPY outside the film can be easily detected by the appearance of the film surface which gradually turns from having a shiny appearance to charcoal black as t_p exceeds 20 min. For this reason, the electrochemical method of preparing the composite becomes less attractive beyond 20 min of treatment.

Measured values of the parallel conductivity σ_{\parallel} and transverse conductivity σ_{\perp} are shown in Figure 1. These values have been corrected to reflect the change of film thickness upon polymerization treatment. The distribution of parallel conductivity across the film thickness is not uniform in both types of film. Measurements showed that while the film surface on the electrode side became conductive very quickly, the free surface near the solvent did not change its conductivity until a pure PPY layer began to form at the free surface of the film; consequently, only the σ_{\parallel} data of the most conductive side (near the electrode) are shown in Figure 1.

As expected, the parallel conductivities of both electrolyte-blended and unblended films behave in an almost similar manner, rising by about 15 orders of magnitude within the first few minutes and levelling off quickly. By contrast, the corresponding transverse conductivities differ markedly in their time dependence during the first 30 min of reaction. Thus, while the σ_{\perp} value for the blended film rises sharply by about six orders of magnitude within 2 min, the corresponding value for the unblended film remains dormant for almost 15 min before it rises and approaches that of the blended sample. Since, for $t_p > 20$ min, a conductive pure PPY layer begins to form at the free surface of the film, it is obvious that the PVC film has been transformed into a highly inhomogeneous composite by the time its transverse conductivity approaches an equilibrium value. The equilibrium values of σ_{\parallel} and σ_{\perp} are respectively *ca.* 10 and 10^{-2} S cm⁻¹ for the treated PVC-TEAFB film and 2.5 and 10^{-3} S cm⁻¹ for the treated PVC film. These values are to be compared with 10 and 10^{-1} S cm⁻¹ for a pure PPY film prepared under the same conditions but without the PVC coating on the electrode.

The initial increase of σ_{\parallel} in Figure 1 is undoubtedly due to the ability of the electrolytic solution and pyrrole to move rapidly across the film thickness and initiate the electrochemical synthesis of the conductive polypyrrole near the electrode. Once a conductive PPY network layer is formed inside the film, the layer should begin to grow at the expense of the pure PVC region by continuous accretion of both pyrrole and electrolyte and polymerization of the monomer at its boundary. However, while the σ_{\perp} data in Figure 1 suggest that the rates of polymerization and growth of the conductive layer during the first 20 min may be much higher in PVC-TEAFB film than in PVC film, this is not borne out by our thickness expansion measurements which show the amounts of uptake to be about the same in both films. Instead, it appears that the rapid increase of σ_{\perp} in the PVC-TEAFB film might result from a more uniform distribution of the

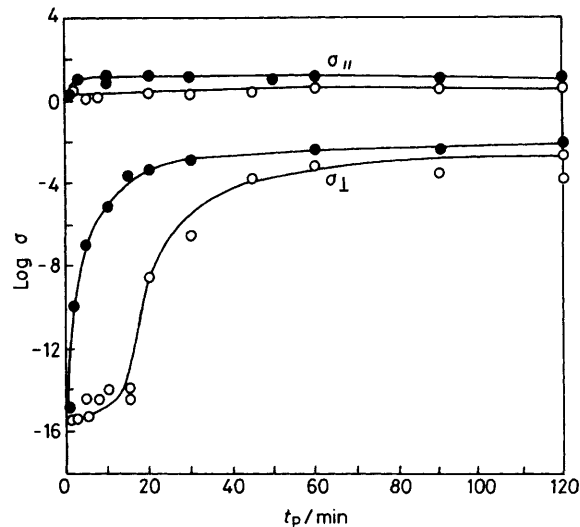


Figure 1. Plots of conductivities measured along the surface direction σ_{\parallel} , and across the thickness σ_{\perp} , as functions of polymerization time t_p for the PVC film (○) and PVC-TEAFB film (●).

conductive PPY network inside the film because of the preponderance of electrolyte already mixed with PVC. This is further supported by the following two observations. Firstly, whereas the treated PVC-TEAFB films never delaminated, the PVC films that had been treated for 5 to 20 min tended to split into two layers when lightly rubbed at the surface, the layer near the solvent side being transparent and nonconductive and the other being dark and conductive. Secondly, as the thickness of the film is increased, say, from 1.5 μ m to 3.0 μ m, the σ_{\perp} curve for the PVC-TEAFB film shifts by only *ca.* 10 min to the right on the time axis; by contrast, the corresponding curve for the PVC film shifts by *ca.* 90 min. These observations tend to confirm that while the uptake of pyrrole and electrolyte in both types of film may be the same at a given reaction time, the resulting conductive network is distributed much more uniformly in the PVC-TEAFB film than in the PVC film. While the exact mechanism has not been established, it seems that the greater uniformity of conductivity in the blended film is brought about by the high concentration of electrolyte which induces not only a sharper drop of electrical potential near the electrode but also a more rapid propagation of the conductive network before the pure PPY layer begins to form at the film surface.

In summary, we have demonstrated that by adding an electrolyte to the host polymer prior to the electropolymerization of pyrrole, it is possible to improve substantially the uniformity of the conductive property in the resulting polymer composite within a short reaction period. While our study has been carried out on the PVC-TEAFB-pyrrole system, it is quite obvious that the same technique can be applied with equal success to other systems (*e.g.*, PVC-TEAFB-thiophene).

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