Polymer Journal, Vol. 18, No. 1, pp 95—98 (1986)

SHORT COMMUNICATIONS

Highly Transparent and Conducting Polypyrrole–Poly(vinyl alcohol) Composite Films Prepared by Gas State Polymerization

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(Received May 21, 1985)

KEY WORDS Transparent Film / Conducting Polymer / Polypyrrole / Poly(vinyl alcohol) / Composite Film / Gas State Polymerization /

Recent years, improvements of mechanical property, processability, and stability in atmospheric environment for the conducting polymer have been made by forming polymer polymer composites.[1–4] For example, blending of polyacetylene with other polymers,[1] synthesis of block copolymers containing acetylene[2] and electrochemical polymerization of pyrrole on a modified electrode by polyacetylene[3] or other insulating polymers[4] have been extensively reported. Among them, the electrochemically polymerized composites of polypyrrole have attracted much attention due to the excellent properties of stability and flexibility. On the other hand, pyrrole can be polymerized chemically by oxidizing agents. Angeli and Lutri[5] observed for the first time that pyrrole with hydrogen peroxide in acetic acid formed a black precipitate which was named pyrrole black. Pyrrole blacks are also obtained by use of other oxidizing agents, such as nitrous acid,[6] lead dioxide,[7] ferric chloride,[8] quinones,[9] diazonium salts,[10] ozone[11] and potassium persulfate.[12]

In our laboratory, it has been found that the conducting composite films of polypyrrole can be simply prepared by exposing polymeric matrix films containing ferric chloride to pyrrole vapour. Our composite films are, moreover, highy transparent under the appropriate preparation conditions. In this communication, the conductivity and the transparency of polypyrrole composite films by the gas state polymerization, are discussed.

Poly(vinyl alcohol) (PVA; $M_n = 22000$) was used as a polymeric matrix. $FeCl_3$ was an oxidizing agent for the polymerization. After dissolving PVA and $FeCl_3$ in water, the solution was cast on a poly(ethylene terephthalate) film substrate. The preparation of polypyrrole–PVA composite films was carried out in a desiccator at −15°C by exposing PVA films containing $FeCl_3$ on the PET film to pyrrole and H_2O vapours which had been deoxygenated sufficiently. The polymerization period was from 30 min to 24 h. The composite films were then dried under vacuum at room temperature. Conductivity measurements were performed under vacuum by the fourprobe technique at room temperature. The transparency of the polypyrrole–PVA composite on the PET film was estimated by UV double beams spectrometer with using a PET film as a

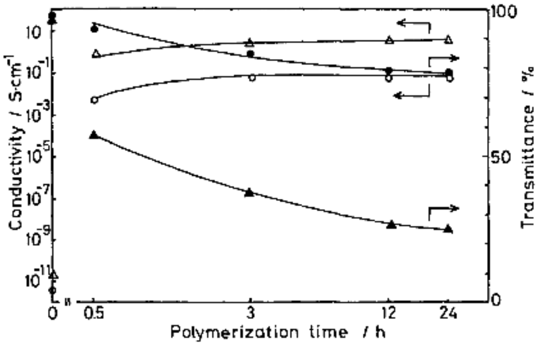

Figure 1. Polymerization time dependence of the conductivity and transmittance of polypyrrole–PVA composite films: (○, ●), PVA/$FeCl_3$ = 95/5 wt%; (△, ▲), PVA/$FeCl_3$ = 70/30 wt%; composite film thickness, 2 μm; wave length, 550 nm.

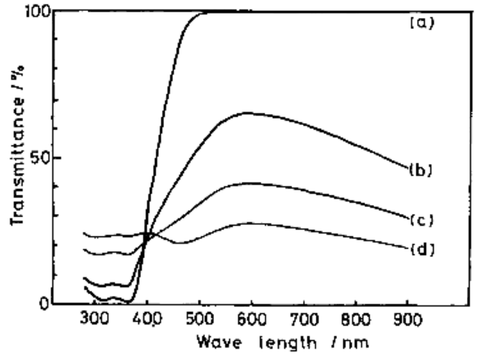

Figure 2. UV-visible spectra for the various polymerization periods: (a), original film before polymerization; (b), 30 min; (c), 3 h; (d), 24 h; PVA/$FeCl_3$ = 80/20 wt%; film thickness, 2 μm.

reference. The transmittance of the only polypyrrole–PVA composite was obtained because the reflection and absorption of the PET film to support the composite were canceled.

Figure 1 shows the variation of the conductivity and the transmittance at 550 nm with respect to the polymerization time for polypyrrole–PVA composite films containing various concentrations of $FeCl_3$. The conductivity increases steeply up 30 min, and then tends to saturate after 30 min, whereas the transmittance decreases gradually without saturation even after 30 min. In the $FeCl_3$ concentration lower than 5 wt%, the composite films show high transparency as well as fairly good conductivity. On the other hand, the transparency decreases at high $FeCl_3$ concentration as 30 wt%. As seen in Figure 1, for example, the composite film corresponding to polymerization time of 24 h shows only 28% transmittance and 8 S cm^{-1} conductivity.

It seems that ion conduction of $FeCl_3$ does not influence conductivity of polypyrrole composite films, because the conductivity of the original film containing 30 wt% $FeCl_3$ before polymerization is 2×10^{-11} S cm^{-1} and nearly equal to that of PVA. As increasing the polymerization time, the color of transparent composite films changes from yellow through greenish yellow finally to brown. Not only the temperature dependence of the conductivity but also the thermopower in a polypyrrole–PVA composite film prepared by this method were similar to those of polypyrrole[13] prepared by the electrochemical polymerization method. The polypyrrole–PVA composite films of polymerization time of 24 h were so stable that the conductivities hardly decrease even after six months' exposure in air at room temperature.

Figure 2 shows UV-visible spectra of polypyrrole–PVA composite films with 20 wt% $FeCl_3$ for various polymerization periods. With the increase of polymerization time, the transmittances of the composite films increase in near ultraviolet region and decrease in near infrared region. The spectral changes in the region of 300—400 nm are due to the reduction of Fe^{3+} to Fe^{2+}. The absorption bands above 800 nm suggest the formation of free carrier and the new absorption band in 400—500 nm for the polymerization time of 24 h is due to π–π^* transition.[14]

The relationships among the conductivity, the transmittance and the concentration of $FeCl_3$ are shown in Figure 3. The conductivity of the composite film becomes saturated above 20 wt% $FeCl_3$ while the transmittance decreases with the increase of $FeCl_3$ concentration. Figure 4 shows UV-visible spectra of polypyrrole–PVA composite films of polymerization time of 24 h for various $FeCl_3$ concentrations. The spectra of the both samples with 20 wt% and 30 wt% $FeCl_3$ are almost similar to each other, which corresponds that the conductivity is saturated above $FeCl_3$ concentration of 20 wt%. In forming a highly transparent and conducting composite film, the optimum conditions of $FeCl_3$ concentration and polymerization time are 5 wt% and 24 h or 30 wt% and 30 min, in our experiments.

Because a polypyrrole film prepared by electrochemical polymerization has an absorption band in visible-near infrared region, the film colour is near black. Thus, the visible light can not pass through the electrochemically polymerized film with the thickness of *ca.* 2 μm. Recently Tamamura *et al.*[4] have reported that transparent and conducting polymer films were prepared by the electrochemical formation of polypyrrole–polymer composites. But, the gas state polymerization can improve the transparency without decreasing the conductivity compared with the electrochemical polymerization. Another characteristic for the gas state polymerization is the simplicity in processing because of the dry system.

Scanning electron micrographs display the

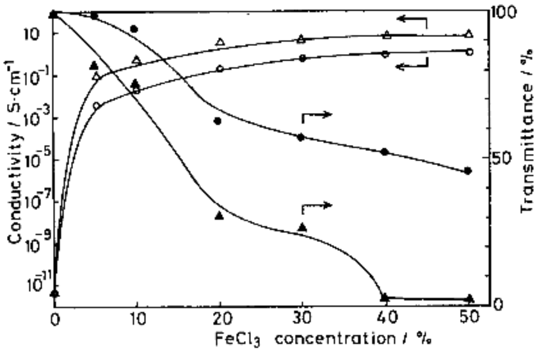

Figure 3. $FeCl_3$ concentration dependence of the conductivity and transmittance of polypyrrole-PVA composite films: (○, ●), 30 min, polymerization time; (△, ▲), 24 h; composite film thickness, 2 μm; wave length, 550 nm.

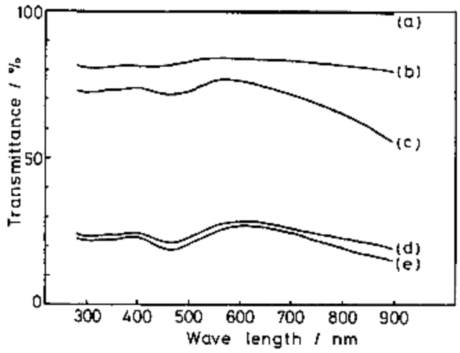

Figure 4. UV-visible spectra for the various $FeCl_3$ concentrations: (a) PVA film; (b), PVA/$FeCl_3$ = 95/5 wt%; (c), 90/10 wt%; (d), 80/20 wt%; (e), 70/30 wt%; polymerization time, 24 h; film thickness, 2 μm.

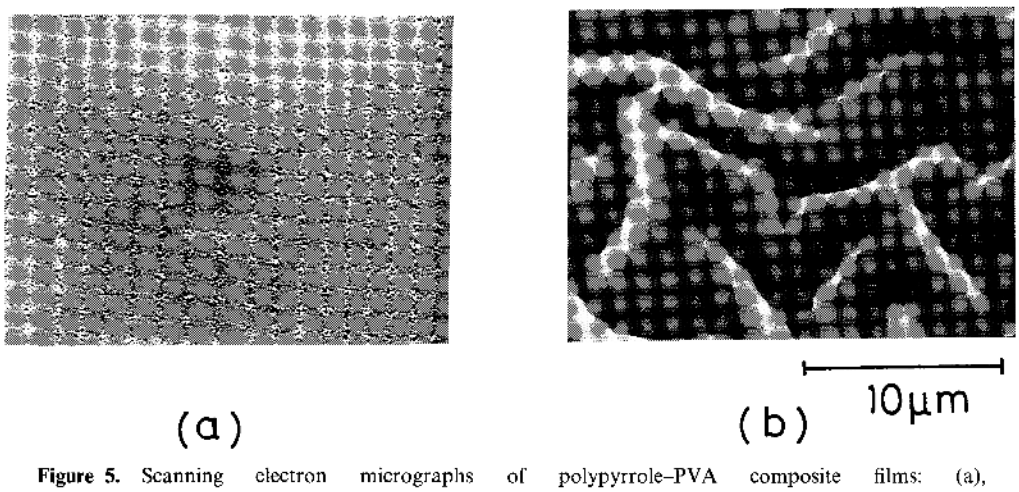

Figure 5. Scanning electron micrographs of polypyrrole–PVA composite films: (a), PVA/$FeCl_3$ = 90/10 wt%; (b), 70/30 wt%; polymerization time, 24 h.

highly flat surface for the film of 10 wt% $FeCl_3$ (a), but the extremely rough surface for the film of 30 wt% $FeCl_3$ (b) as shown in Figure 5. It is obvious that the surface morphology affects greatly the transmittance of the composite film. When samples with rough surfaces were coated by transparent polymers, such as poly(methyl methacrylate), poly(vinyl acetate) or poly(vinyl alcohol), the transmittances increased remarkably from less than 10% up to 30—50%. This experimental result suggests that the $FeCl_3$ concentration plays very important role on the surface formation of the composites.

It is concluded that the highly transparent and conducting polypyrrole–PVA composite films can be easily obtained by exposing PVA films containing ferric chloride to pyrrole vapour. This technique of the gas state polymerization is a very good tool for obtaining transparent and conducting polymer. The present finding might accelerate the use of the polypyrrole composite as a new functional material.

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