

Preparation and morphology of electrically conductive and transparent poly(vinylchloride)-polypyrrole composite films

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Summary

The chemical process of preparing poly(vinylchloride)-polypyrrole composite films with high electrical conductivity and transparency has been studied. Pyrrole has been diffused into the poly(vinylchloride) matrix in the swelling medium of n-hexane and acetone mixture. The oxidative polymerization of the diffused pyrrole in the binary solvent system of acetonitrile and methanol gives high conductivity of the polypyrrole as well as the good penetration of the oxidant into the PVC polymer matrix. The analytical testing of the composite film shows the formation of homogeneous mixture of polypyrrole and poly(vinylchloride) conductive layer within the 1.0 μ m of thickness on the film surface. The transparency of the composite film showed about 50~60% at 500 nm. The electrical conductivity of the composite was about 20 s/cm.

Introduction

Conducting polymers have drawn much interests during the last decade because these polymers are considered as highly promising new materials for electronic devices, electrical applications, electrochromic displays, polymer batteries, polymer modified electrodes, and functional membranes. Since the discovery of high conductivity in polyacetylene upon doping with iodine(I₂) or arsenic pentafluoride(AsF₅) in the late 1970s, variety of new conducting polymers such as polypyrrole, polythiophene, polyaniline, polyindole, polyazulene, etc have been prepared and extensive studies on chemical, physical, morphological, and electronic/electrical properties of these polymers have been conducted[1-8]. Among these conducting polymers polypyrrole has recently attracted much attentions because of its high electrical conductivity combined with its overall stability in doped state.

In recent years significant researches have been reported on highly conductive polypyrrole synthesized by methods of electrochemical polymerization, chemical polymerization, chemical vapor polymerization, and photo-electrochemical polymerization[9-16]. All these polymerization methods readily produce conductive polypyrrole and the polymer shows overall stability under ambient conditions.

The polypyrrole film prepared chemically or electrochemically in organic solvent containing electrolyte exhibits a conductivity up to 500 s/cm, which is a sufficient electrical conductivity for the most of the applications. Unfortunately, however, these films show poor mechanical properties as well as the lack of processability. This is one of the reason for their limited utilization despite of promising new materials of potential applications. Forming composite films with the conventional plastic materials offers the solutions of these

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problems[17-20].

In this study transparent and highly electrically conductive poly(vinyl chloride)-polypyrrole composites have been prepared using the chemical diffusive polymerization method. The chemical process to produce the composite has been investigated and studies on chemical, morphological, and electrical properties of these composites have been conducted by utilizing various analytical techniques such as FT-IR, SEM, TEM, and ESCA.

Experimental

Preparation of Poly(vinyl chloride)-Polypyrrole Composite Films

The chemical oxidative polymerization of pyrrole yields a conductive black powder and its process has been known for many years. This process is particularly simple and readily takes place with a variety of oxidizing agents in both solution and vapor phase. Although the chemical oxidative polymerization usually leads to polypyrrole powders, composite films can be processed by allowing the oxidative polymerization to take place in PVC matrix with diffused pyrrole. In this process the PVC film was immersed in a swelling solution containing pyrrole so that the pyrrole monomer could diffuse into the polymer matrix and then subsequently polymerized in an oxidative solutions containing oxidant in a binary solvent system of similar solubility coefficients with PVC film.

1. Preparation of diffusion solution

The solubility coefficients of acetone and acetonitrile are similar to chlorinated polymers, such as PVC. Thus solutions of pyrrole in these solvents easily swell PVC and make it possible to prepare the composites with polypyrrole. In these systems the major portion of solutions consisted with non-solvent for PVC. This technique allows to use the cheap less toxic chemical as a major medium for the diffusion solutions. Mixture of acetone, n-hexane and pyrrole was chosen as a diffusion medium because it yields highly conductive and transparent composite film with good processability. The typical composition of diffusion solution for the processing of transparent conductive composite films is as follow;

n-hexane : 87.8 vol%
 Acetone : 9.8 vol%
 Pyrrole : 2.4 vol%

2. Evaporation of the excessive diffusion solution from the surface

After the immersion into the diffusion solution it is necessary to remove the excessive pyrrole from the surface of the PVC film to allow the polymerization to proceed inside the polymer matrix rather than surface of the film. With a relatively short evaporation time a large amount of pyrrole monomers were polymerized on the surface of the film. For the typical process of practical purpose the evaporation time of 30 to 60 seconds in the air will allow evaporating most of the pyrrole monomer adsorbed on the film surface and thus the oxidant could diffuse with less retardation into the polymer matrix where the composite forms. However, the evaporation time needs to be adjusted with the vapor pressure of the each solvent used and the environmental conditions of the drying process.

3. Oxidative polymerization of pyrrole

The oxidative polymerization of pyrrole takes place in a 1.0 mole FeCl₃ solution of binary solvent system with acetonitrile and methanol. The oxidation solution requires the capability of swelling PVC for promoting the deeper penetration of oxidant into the polymer matrix. For the mixture of acetonitrile and methanol with 1.0 mole FeCl₃ oxidant the mole

fraction of acetonitrile determines the compatibility with the swollen PVC as well as the level of the oxidation potential.

The polymerization reaction proceeds rapidly at a higher oxidation potential since the reaction rate is determined by the electron transfer rate between the pyrrole monomer and Fe^{3+} ion. The oxidation potential level of this binary solvent system can be adjusted within the range of 1365 mV (measured with 100% acetonitrile) to 560 mV (measured with 100% methanol). Considering the oxidation potential of pyrrole monomer with this binary solvent system being in the range of 600–890 mV the mole ratio of acetonitrile may be changed in the range of 1.0 to 0.75 in which the pyrrole monomer could be oxidized above its own oxidation potential. The mole ratio of acetonitrile needs to be adjusted in this range with the solvent systems used in the diffusion process. The mole ratio of 85/15 of acetonitrile/methanol resulted high electrical conductivity of the composite film with the solvent system of n-hexane, acetone, and pyrrole when polymerized at 0°C. The oxidation potential also varies with the amount of oxidant (FeCl_3) as well as with the reaction temperature.

The oxidative polymerization was carried out in the ice bath to keep the polymerization temperature close to zero degree. The polymerization temperature affects the molecular structure of polypyrrole, conjugation length, and the dopant level. The nature and extent of chemical defect sites and charge distribution characteristics of polypyrrole will be affected with the temperature of the polymerization. It is well known that polypyrroles synthesized under lower temperature below 0°C has longer conjugated chain length with well defined oriented structures of less defect which results in high electrical conductivity.

Results and Discussion

Effect of Diffusion Time

As the PVC film is immersed into the diffusion solution which contains solvents of similar solubility coefficient, the poly(vinylchloride) film will be swelled to allow the pyrrole monomer to be diffused into the polymer matrix. The thickness of conducting layer in the composite film will be significantly varied with the dipping time allowed for the diffusion of pyrrole. In general, the longer the dipping time is, the thicker is the conducting layer of the composite film. For the good transparency of the processed composite film, diffusion time of 4 to 6 minutes was needed and it resulted in about 1.0 μm thickness of conducting layer with the composite conductivity as high as 20 S/cm.

Fig. 1 shows the effect of diffusion time on the surface resistance of the PVC-polypyrrole composite film. With the prolonged dipping time of about two hours in the diffusion solution completely black composite films could be obtained showing high electrical conductivity with some flexibility of the film.

Morphology of the Composite Film

The poly(vinylchloride)-polypyrrole composite films were examined with SEM and TEM microscopes. It was clear with the TEM examination that the conducting layer exists on the surface of the PVC film with the thickness of about 1.0 μm on both sides [Fig. 2]. The conducting layer consists with the composite of polypyrrole and PVC with the polypyrrole mole ratio of 64% determined from the atomic ratio of N with the X-ray photoelectron spectroscopy. It is observed under the microscope that the conducting layer exists as a homogeneous mixture of polypyrrole and PVC polymer as shown in Fig. 2. The polypyrrole particles are uniformly dispersed in the conducting layer and form a network of conducting path.

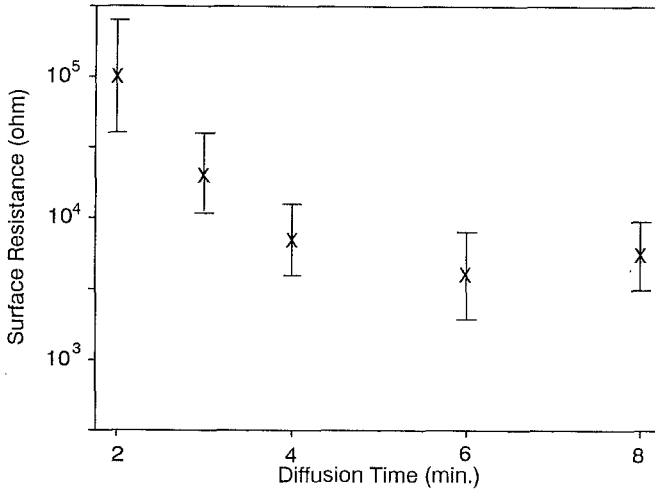


Fig. 1 Effect of diffusion time on the surface resistance of composite film in the solvent mixture of n-hexane, acetone and pyrrole.

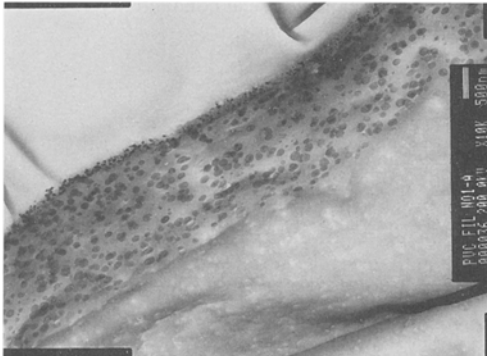


Fig. 2 TEM photograph of poly(vinylchloride)-polypyrrole composite film showing conductive layer of 1 μm thickness ($\times 10,000$).

Electrical Conductivity of the Composite Film

The electrical conductivity of the composite film was measured with the standard four-probe method. The electrical conductivity is given as;

$$\sigma = 0.2206 \times \frac{i}{v \times d}$$

where, σ is the conductivity in s/cm.

v is the applied potential in volt.

d is the thickness of the conducting layer in cm.

i is the current in ampere.

The typical conductivity of the composite film shows about 20 s/cm with the 50–60% transparency at 500 nm. The pure polypyrrole layer which is synthesized under the same conditions as the poly(vinylchloride)-polypyrrole composite and measured with the thin disk pressed from the precipitate of the polypyrrole showed the electrical conductivity of about 250 s/cm. For the application of antistatic plastics a critical conductivity exists to give enough antistatic performance to the plastics. According to Matsui and Tsutsumi[21] the critical point has been identified with the electro-conductive fiber filled with carbon black or metallic compound as high as 10^9 ohm cm of volume resistivity. This is the conductive range to prevent corona discharge which occurs at the static voltage accumulation of more than 2 kV with the conductive fiber.

The poly(vinylchloride)-polypyrrole composite film with the conductive layer of $1.0\mu\text{m}$ thickness shows the electric resistance of about 10^4 ohm/cm, which is far more conductive than the critical point by several orders of magnitude. The conductivity of the composite film can be increased up to the range for the application of the electromagnetic interference shield.

Transparency of the Composite Film

The composite film with $1.0\mu\text{m}$ of conducting layer exhibits excellent transparency[Fig. 3]. The transmittance of this film shows about 50–60% at 500 nm. As the thickness of conductive layer increases the composite film become less transparent.

FTIR/ATR Studies

IR spectrum of poly(vinylchloride)-polypyrrole composite film shows the characteristic peaks of both PVC and polypyrrole[Fig. 4]. The featureless decrease in absorption from 4000 to 1700 cm^{-1} has been assigned to be the tail of absorption band located in the NIR region same origin as in the pure polypyrrole except the small absorption peak located at 2920 cm^{-1} which originates from the C-H stretching mode of PVC. The spectrum shows the characteristic bands of polypyrrole at 1550 , 1320 , 1180 , 1040 , 900 cm^{-1} and those of flexible PVC located at 2920 , 1730 , 1430 , 1250 , 1100 , 970 cm^{-1} . However the absorption spectrum below 1700 cm^{-1} has been dominated by the polypyrrole moiety. The IR absorption spectrum

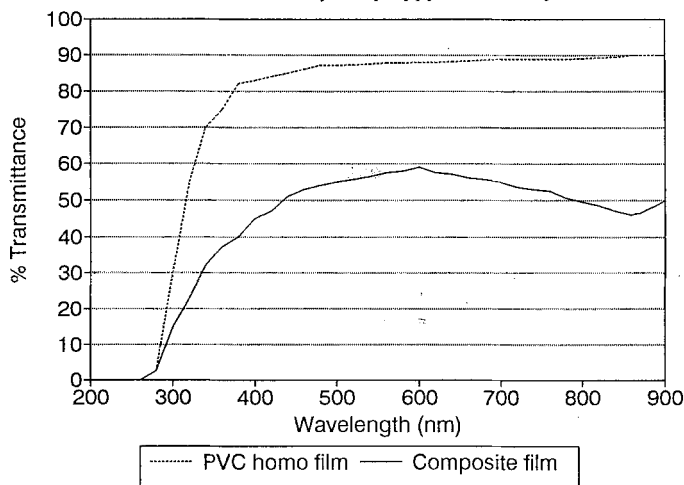


Fig. 3 Transparency of flexible PVC homo film and conductive poly(vinylchloride)-polypyrrole composite film.

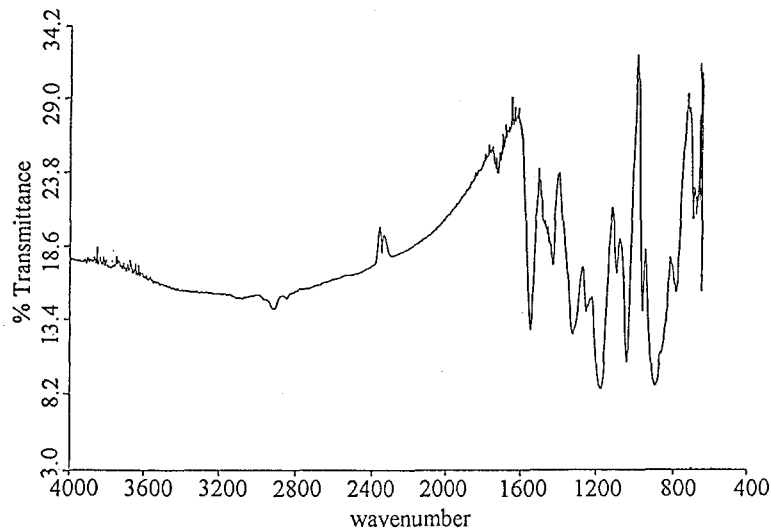


Fig. 4 IR spectrum of poly(vinylchloride) - polypyrrole composite film.

confirms the formation of homogeneous composite structure of poly(vinylchloride) and polypyrrole.

Conclusions

The process of preparing transparent and highly electrically conductive composite film of poly(vinylchloride)-polypyrrole has been studied. The solvent system of n-hexane, acetone, and pyrrole mixture offers effective swelling medium of PVC film for preparing composite film.

The oxidative polymerization of the diffused pyrrole in the binary solvent system of acetonitrile and methanol gives high conductivity of the polypyrrole as well as the good penetration of the oxidant into the polymer matrix. The mole ratio of acetonitrile to methanol in the binary solvent system with 1.0 mole of FeCl_3 showed optimum in the range of 0.80 to 0.85.

The thickness of the conducting layer in the processed PVC film was measured to be about $1.0\mu\text{m}$. The mole ratio of polypyrrole to the PVC matrix in this conducting layer was estimated to be about 64%. The analytical testing of the composite film shows the formation of homogeneous mixture of conductive layer within the $1.0\mu\text{m}$ of thickness on the film surface. The transparency of the composite film showed about 50–60% at 500 nm.

The electrical conductivity of the composite film was measured as high as 20 s/cm. The conductivity of the composite can be increased by allowing longer treatment time, which will in turn increase the volume fraction of the polypyrrole in the composite. Thus the conductivity of the PVC composite film can be increased up to the range of electro-magnetic interference application with the process developed in this study.

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