

< 研究論文 (學術) >

전도성 Cellulose Acetate/Polypyrrole 복합체의 제조와 전기적 성질

박연흠·방호주*

성균관대학교 공과대학 섬유공학과
(1990. 2. 23 접수)

Preparation and Electrical Properties of Conducting Cellulose Acetate/Polypyrrole Composites

Yun Heum Park and Ho Joo Bang

Dept. of Textile Eng., College of Eng., Sung Kyun Kwan Univ., Su Won, Korea

**Present Address: Sam Yang R & D Center, Jeon Ju, Korea*

(Received February 23, 1990)

요약—산화제를 함유한 셀룰로우스 아세테이트 필름을 피롤 증기 속에 노출시킴으로써 전도성 셀룰로우스/폴리피롤 복합체 필름을 합성하고 폴리피롤의 형성을 IR 및 전자현미경을 사용하여 확인했다. 복합체 내에 존재하는 폴리피롤의 형태는 사용한 산화제의 종류에 따라 다르게 나타났다. 산화제로 사용한 몇 가지 금속염화물 중에서 염화제 2철이 높은 전도도를 가지는 복합체를 합성하는데 가장 효과적이며 50중량 퍼센트의 염화제 2철을 첨가해서 제조한 복합체 필름의 전기전도도는 10^{-2} S/cm에 달한다.

Abstract—The electrically conducting cellulose acetate/polypyrrole composite films were synthesized by exposing cellulose acetate film containing oxidizing agent to pyrrole vapour and the formation of polypyrrole is confirmed by IR and electron microscopic studies. The morphologies of polypyrrole in the composites are different depending on the oxidizing agent. Ferric chloride is most effective among several metallic chlorides to synthesize the composites with high electrical conductivity. The conductivity of composite films synthesized with 50 wt.% of ferric chloride reaches upto 10^{-2} S/cm.

Introduction

Two major impediments to the utilization of electrically conducting polymers have been poor atmospheric stability and processability. However, polypyrrole has attracted great interest for its good conductivity and high stability.¹⁾ The polypyrrole films, either homogeneous or composite, are prepared by electrochemical oxidative polymerization. But the procedure of electrochemical polymerization is more or less complicated and the area of the prepared films depends on that of electrodes, so that it is difficult to prepare large area

films by that method. On the other hand, polypyrrole is also prepared by the chemical oxidative polymerization. However polypyrrole prepared by chemical polymerizations is usually formed as bulky powders and is poor in conductivity.²⁾

In order to improve the poor mechanical properties of polypyrrole and prepare in the form of film which is attractive for technical applications such as membrane switches and flexible circuitry, we have prepared a conducting composite material by the vapor-phase polymerization of pyrrole in an insulating polymer matrix. Cellulose acetate was chosen as a matrix polymer because the remain-

ing hydroxyl group in cellulose acetate can form the complex with metal salt³⁾ which plays the role of site for the polymerization of pyrrole and thus the distribution of polypyrrole and the resulting conductivity of the composite is uniform throughout the composite.

Experimental

Materials and chemicals

Cellulose acetate which contains 2.3 acetyl groups per glucose residue was obtained from Sun Kyung Industries as a form of flake. All Chemicals used in this work such as acetone (Yakuri Chem. Co.), acetic acid (Kokusan Chem. Co.), ferric chloride (Sigma Chem. Co.), cupric chloride (Junsei Chem. Co.), nickel chloride (Junsei Chem. Co.) and pyrrole (Sigma Chem. Co.) were special reagent grade and used without further purification.

Preparation of cellulose acetate (CA)/polypyrrole (PPY) composite films

Cellulose acetate was washed several times with ethanol and distilled water in the Soxhlet apparatus and dried. Dried CA was dissolved in acetone or acetic acid (10% w/v). A required amount of oxidizing agent (ferric chloride and cupric chloride dissolved in acetone, respectively and nickel chloride dissolved in acetic acid) was added to CA solution by means of a syringe. After thorough mixing, the oxidizing agent-impregnated CA solution was cast in the form of film. A cosolvent was removed under vacuum at room temperature. The preparation of CA/PPY composite films was carried out at room temperature by exposing oxidizing agent-impregnated CA film to pyrrole vapour. The fully solvent-evacuated composite films were 10-30 μm thick and were strong, flexible and semitransparent with a block colour.

Measurement of electrical conductivity

Conductivity measurements were made using four-probe techniques. The distance between neighboring probes was 5 mm.

Results and Discussion

In order to confirm the formation of polypyrrole in the oxidizing agent-impregnated CA films, IR and electron microscopic studies have been carried out for the composite films synthesized by varying the polymerization time of pyrrole.

Fig. 1 shows the FT-IR spectra of CA/PPY composites. The spectra were taken via a Nicolet DX FT-IR spectrophotometer. The characteristic absorption peak near 1550 cm^{-1} corresponds to the NH band of pyrrole ring.⁴⁾ In comparison with the characteristic absorption peaks of (A), (B), and (C) in Fig. 1 near 1550 cm^{-1} , the intensity of peak becomes stronger as the polymerization time of pyrrole becomes longer. Thus it is indicated that pyrrole has been polymerized in ferric chloride-impregnated CA films.

For the investigation of surface morphology of CA and CA/PPY composite films, the scanning electron micrographs were taken using a JEOL JSM-35CF scanning microscope. The surface morphology of the oxidizing agent-impregnated films does not have any distinct surface structure irrespective of the kind of oxidizing agent as shown in Fig. 2a. The ferric chloride-impregnated CA film exposed to pyrrole vapor for 1 hr shows smooth

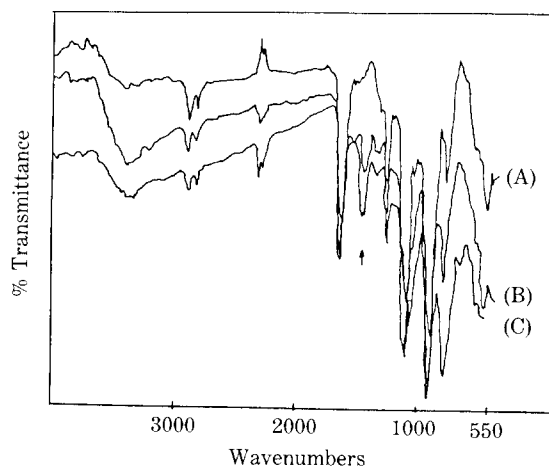
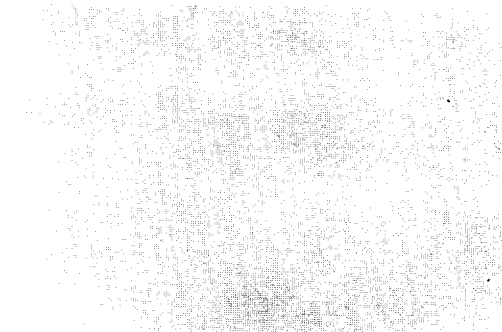
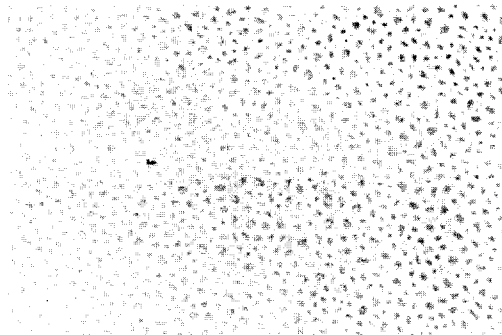


Fig. 1. FT-IR spectra of CA/PPY composite films synthesized with 50 wt.% of FeCl_3 for 10 min. (A), 2 hrs (B), and 3 hrs (C).

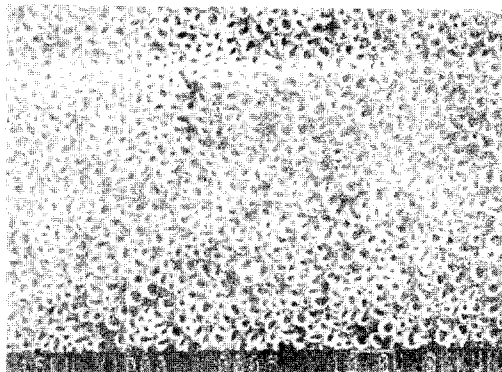
structure (Fig. 2b). But the film exposed to pyrrole vapor for 3 hr shows the structure jutting out of the smooth surface (Fig. 2c). The surface morphology of CA/PPY films has very different structure depending on the kind of impregnated



(a)×1000



(b)×1000

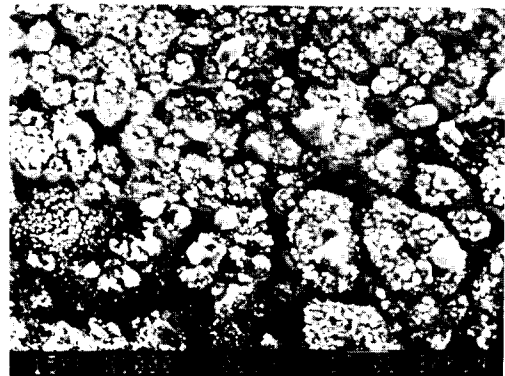


(c)×1000

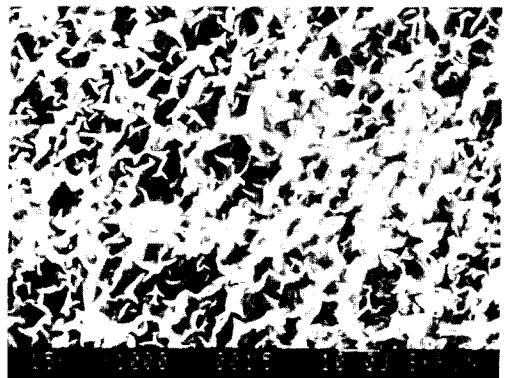
Fig. 2. Scanning electron micrographs of CA films containing 50 wt.% of FeCl_3 ; before exposing to pyrrole vapour. (a), after exposing to pyrrole vapour for 1 hr (b), and 3 hrs (c).

oxidizing agent as shown in Fig. 3. Comparing with the surface structures of Fig. 2c, Fig. 3a and 3b, PPY synthesized with ferric chloride has more compact structure and the gaps between PPY phases are closer than the other two PPY structures. This difference in surface morphology has resulted in the difference in the electrical conductivity of CA/PPY composite films as shown in Fig. 4. It is supposed that the closer the gaps between the conducting components the higher the electrical conductivity. Fig. 4 is in good agreement with the supposition.

Fig. 5 (A), 5 (B), and 5 (C) show the conductivity as the functions of the polymerization time of pyrrole and the concentration of oxidizing agents; ferric chloride, cupric chloride, and nickel chloride



(a)



(b)

Fig. 3. Scanning electron micrographs of CA films after exposing to pyrrole vapour for 3 hrs; sample films synthesized with 50 wt.% of CuCl_2 (a) and 50 wt.% of NiCl_2 (b).

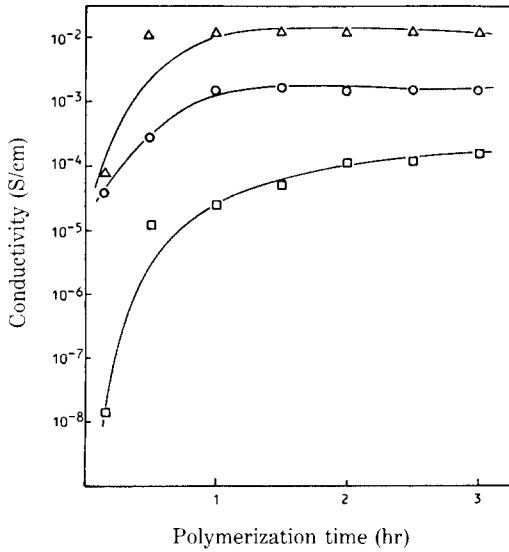


Fig. 4. Electrical conductivity of CA/PPY composite films synthesized with 50 wt.% of FeCl₃ (△), CuCl₂ (○), and NiCl₂ (□).

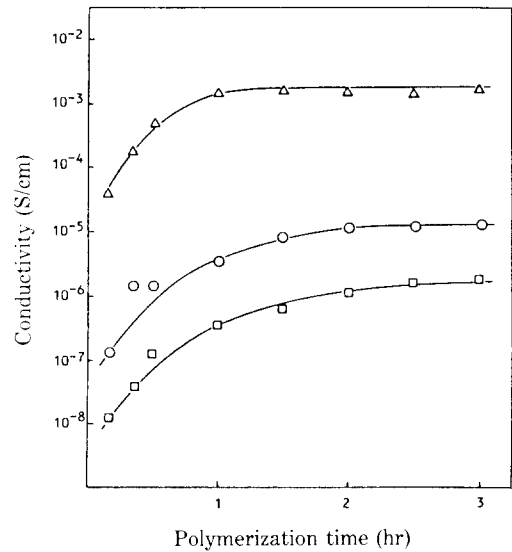


Fig. 5 (B). Electrical conductivity vs. polymerization time of pyrrole at concentrations of 50 wt.% (△), 30 wt.% (○), and 10 wt.% (□) of CuCl₂.

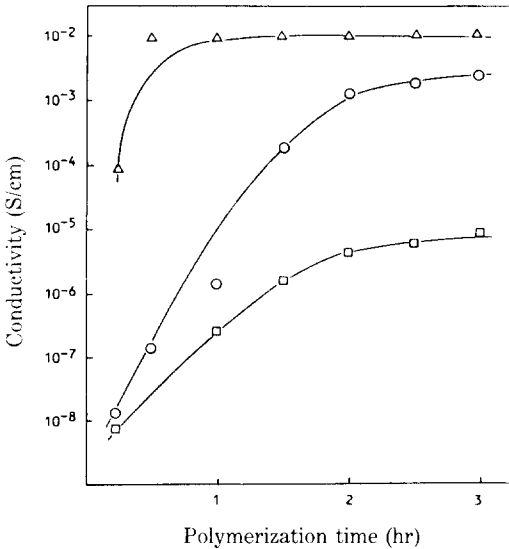


Fig. 5 (A). Electrical conductivity vs. polymerization time of pyrrole at the concentrations of 50 wt.% (△), 30 wt.% (○), and 10 wt.% (□) of FeCl₃.

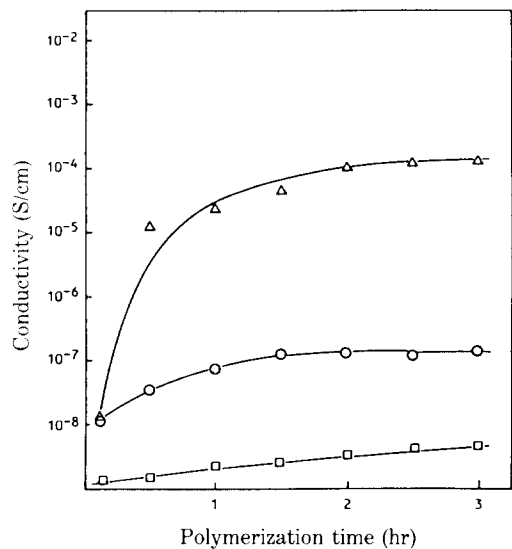


Fig. 5 (C). Electrical conductivity vs. polymerization time of pyrrole at the concentrations of 50 wt.% (△), 30 wt.% (○), and 10 wt.% (□) of NiCl₂.

respectively. The conductivity of the oxidizing agent-impregnated CA films containing no PPY is 10⁻⁹-10⁻¹⁰ S/cm within 0-50 wt.% of the concentration of oxidizing agent. The colour of composite

film changed to black indicating the formation of PPY in the CA film. The conductivities of composite films with 50 wt.% of ferric chloride (Fig. 5 (A)) and cupric chloride (Fig. 5 (B)) increase to

the saturation values of about 10^{-2} and 10^{-3} S/cm, respectively, after one hour of exposure to pyrrole vapour. But for the sample with 50 wt.% of nickel chloride it takes longer time to reach the saturation value, 10^{-4} S/cm. Regardless of the concentrations, ferric chloride is most effective oxidizing agent for the synthesis of PPY and thus obtaining high conductivity among three kinds of oxidizing agents.

In order to investigate the relationship between the conductivity and the amount of PPY formed in composite films, the conductivity and the weight increments of ferric chloride-impregnated CA films after exposing to pyrrole vapour have been measured and the results are shown in Fig. 6. Here, the amount of PPY is represented by the weight increment per 1g of CA film containing required concentrations of ferric chloride. As was expected, the conductivity increases as the amount of PPY formed in CA films increases. We can found remarkable result from Fig. 6, that is, the CA/PPY composite films synthesized under higher concentrations of the oxidizing agent but resulted in containing the same amount of PPY have higher

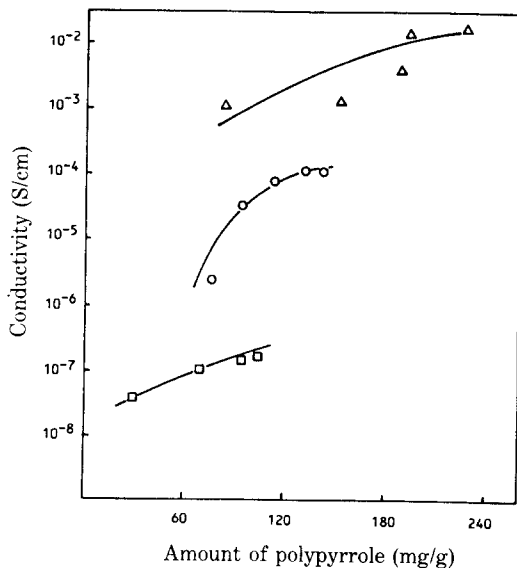


Fig. 6. Relationship between electrical conductivity and amount of polypyrrole; CA/PPY composite films were synthesized with 50 wt.% (Δ), 30 wt.% (\circ), and 10 wt.% (\square) of FeCl_3 .

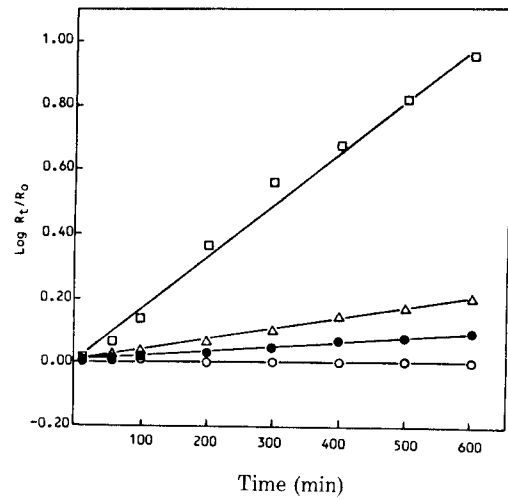


Fig. 7. $\text{Log } R_t/R_0$ vs. time exposed to air at various temperature for CA/PPY composite films.

conductivity. This result is due to the closer insulating gaps between the conducting PPY phases and partly to the conductivity contribution of oxidizing agent. The oxidizing agent functions as the site where PPY is formed. The composite films synthesized under higher concentrations of oxidizing agent have denser site for PPY formation and thus have higher conductivity.

For the investigation of the resistance change according to temperature and time, $\text{log } R_t/R_0$ has been plotted against time under four different temperatures in Fig. 7, where R_t is the resistance at time t and R_0 is the resistance at time zero. At 120°C the resistance of composite film increases very sharply but at the room temperature or below it the resistance change is insignificant. It is supposed that the increase of the resistance is due to longer insulating gaps between PPY phase arising from the thermal motions of polymer molecules.

Conclusion

The vapour-phase polymerization of pyrrole in an insulating polymer matrix, CA opens the possibility to prepare flexible films of composites with a very low content of conducting material. Among the oxidizing agents, such as ferric chloride, cupric chloride and nickel chloride, cupric

chloride is more effective one for the preparation of CA/PPY composites with high electrical conductivity. The composite films synthesized with ferric chloride have the morphology with more compact structure of conducting PPY phases and thus have closer insulating gaps between PPY phase than those synthesized with other oxidizing agents.

After exposing the CA films containing 50 wt.% of ferric chloride to pyrrole vapour for 3 hours, high conductivities upto 10^{-2} S/cm have been obtained. The composite films synthesized with higher concentrations of ferric chloride but containing the same amount of conducting PPY have higher conductivity than that synthesized with lower concentrations of ferric chloride. It is supposed that the denser sites for PPY formation resulting from higher concentrations of oxidizing agent and thus the closer gaps between phases are the major cause for higher conductivity. Under the condition of the room temperature or below it, the resistance of

composite films does not change significantly.

Acknowledgement

The work was supported by the Sung Kyun Academy of Arts and Sciences under Grant 1989. The authors acknowledge this support with thanks.

References

1. A. F. Diaz and K. Kanazawa, "Extended Linear Chain Compounds", J. Miller, Ed., Plenum, New York, Vol.3, p.417 1982.
2. M. Salmon, K. Kanazawa, A. F. Diaz and M. Krounbi, *J. Polym. Sci.* **B20**, 187 (1982).
3. P. Godard, J. L. Wertz, J. J. Bietuyck and J. P. Mercier, *Polym. Eng. Sci.*, **29**(2), 127 (1982).
4. A. Kreutzberger and P. A. Kalter, *J. Org. Chem.*, **65**, 624 (1961).
5. L. A. Samuleson and M. A. Ruy, *Macromolecules*, **19**, 824 (1986).