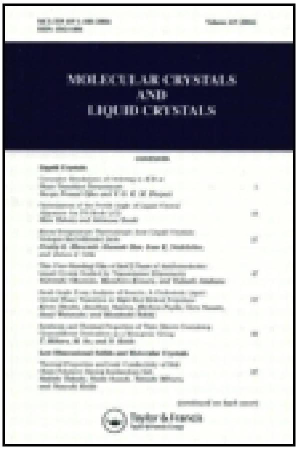

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Structure and Electrochemical Properties of Electrically Conductive Composites

Dong Il Rang [a] , Won Jei Cho [a] & Chang Sik Ha [a]
[a] Department of Polymer Science and Engineering, Pusan National University, Pusan, 609-735, Korea

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STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF ELECTRICALLY CONDUCTIVE COMPOSITES

DONG IL KANG, WON JEI CHO, and CHANG SIK HA[†]
Department of Polymer Science and Engineering,
Pusan National University, Pusan 609-735, Korea

Abstract Conducting composites of polypyrrole(PPy) and poly(N-methylpyrrole) (PNMP) were prepared by electrochemical polymerization of the corresponding monomers at a platinum electrode surface in 0.036M tetrabutylammoniumdodecyl-sulfate(TBADS) / acetonitrile(ACN) electrolyte solution system. Two types of composites were prepared ; PPy/PNMP bilayer composite films and monomer mixture conducting polymer composites of pyrrole and N-methylpyrrole. The composites were characterized by TGA, SEM and 4-probe meter. The composites exhibited different electric resistances and thermal stabilities depending on the preparation method of the conducting polymer composites. The PPy/PNMP bilayer composite films showed lower electric resistance (i.e. better electric conductivity) and higher thermal stability than any other composite films obtained in this work.

INTRODUCTION

Since the discovery of electrochemical polymerization of conducting polymers[1,2], there has been great interest in the electrochemical characteristics of thin conducting polymer films on the electrode surface with respect to both their chemistry and physics, and potential technological applications in electrochromic displays, batteries, and electrochemical sensors[3-5], etc. Recently much attention has been paid to conducting polymers in the field of electronics and electrical engineering[6]. Many studies have focused on the synthesis of conducting polymers, such as polyacetylene, polypyrrole, polythiophene and their derivatives. Among them, polypyrrole (PPy) can readily be obtained in its conducting form by electrochemical oxidation of pyrrole.[7,8]

However, little attention has been paid to bilayer conducting polymer films. The concept of bilayers of polymer films was first introduced by Murray's group.[10] More recently, a few papers concerning bilayer conducting polymer films and conducting polymer composites have been published.[11-14] It has been reported that the electrochemically conductive polymer composite materials possess good electrical and

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[†] To whom all correspondence should be addressed.

mechanical properties.

In this paper, we present the results of the electrochemical, thermal and morphological studies on the polypyrrole(PPy)/poly(N-methylpyrrole)(PNMP) bilayer conducting polymer system and pyrrole/N-methylpyrrole monomer mixture conducting polymer composites using 4-probe meter, thermogravimetric analyzer(TGA) and scanning electron microscopy (SEM).

EXPERIMENTAL

Chemicals Pyrrole and N-methylpyrrole obtained from TCI Chem. Co. were purified by vacuum distillation and stored in the dark at low temperature before use. TBADS was synthesized by reacting tetrabuthylammonium chloride (TBACl) with sodium dodecylsulfate(NaDS) in this laboratory using the method as described in a patent.[15] ACN was of certified analytical grade obtained from Aldrich.

Preparation of bilayer conducting polymer films and monomer mixture conducting polymer composites A platinum electrode (size; 1x1 cm^2) was used for the electrodeposition of bilayer films and monomer mixture conducting polymer composites.

Electrodeposition of bilayer films were prepared in two steps: first, one monomer (pyrrole or N-methylpyrrole) was electropolymerized onto the electrode surface galvanostatically at 20.0 $mAcm^{-2}$ using 0.036M TBADS/ACN electrolyte solution during the 1000 seconds; secondly, the other monomer was also electropolymerized on the previous polymer film layer, which has been covered on the platinum electrode by the same procedures as described above. In this case, the thickness of each layer was equivalent to 20 C/cm^2. Monomer mixture conducting polymer composites were electropolymerized onto the electrode surface galvanostatically at 20.0 $mAcm^{-2}$ using 0.036M TBADS/ACN electrolyte solution containing 0.36M pyrrole and 0.36M N-methylpyrrole monomer, during the 1000 seconds. In the case of the monomer mixture conducting polymer composites, the monomer contents were varied as 1:1, 2:1 and 1:2 by volume/volume.

Measurements The composite films on the platinum electrode were peeled off and throughly rinsed in ACN for a couple of hours. Thermal stabilities of the composite films were examined by TGA(DuPont 2100) at a heating rate of 10℃/min. under N_2 atomosphere. The temperature ranged from room temperature to 800℃. For studies on electric resistance, thin composite films were prepared on a platinum electrode (1 × 1 cm^2) and peeled off. The electrical resistances of the electrode side of the composite films were measured by the standard four-point technique. The morphologies of the electrode side of the composite films were observed by using SEM(JEOL JSM 5200).

RESULTS AND DISCUSSION

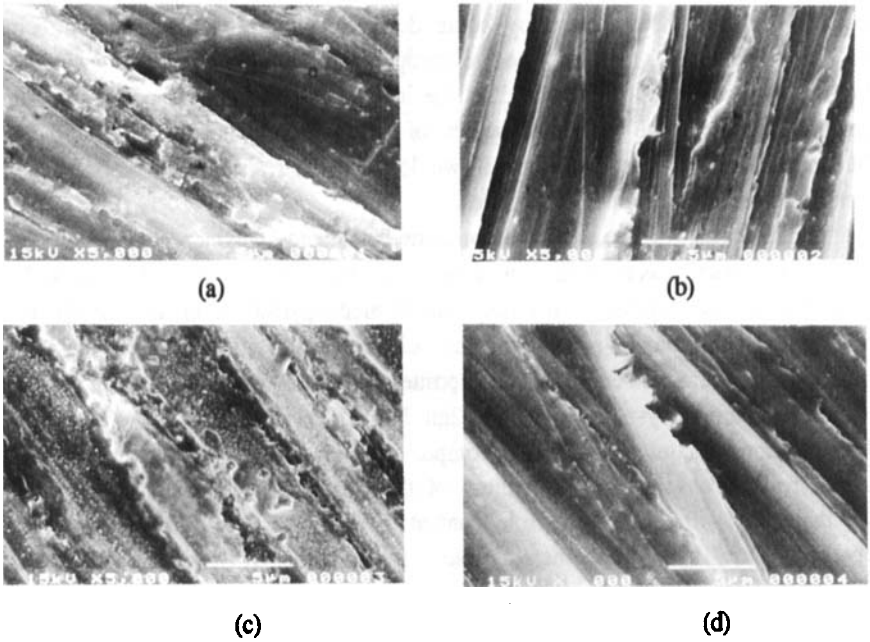
Table 1 shows the resistance values of composites. In general, the electric conductivity should be expressed with σ (S/cm) values, because the resistance varies with the thickness, width, and length of the sample and the deposition efficiency largely depends on the monomer and the polymerization conditions. In this work, however, the resistance values were compared for convenience. It is believed to be acceptable, since the electrode size was fixed (1×1 cm^2) and special care was taken to obtain sample films of uniform thickness throughout the experiments. Bilayer conducting polymer films exhibited different resistance values as compared with homopolymers. We measured the resistance of the electrode side of the films. It was assumed that electrodeposition of PPy onto the PNMP film covered on platinum electrode(PNB) and electrodeposition of PNMP onto the PPy film covered on platinum electrode(NPB) give similar resistance values as those of homopolymers. The results, however, are different from our expectation ; Both PNB and NPB films showed intermediate resistance values between those of their corresponding homopolymers, even though the values are still closer to those of the matrix films on platinum electrode. This indicates that for the bilayer composites the outer layer might interpenetrate into the inner layer on the platinum electrode through the interface by some degree of interaction or reaction between the two homopolymers during the electropolymerization. If there would be no interpenetration of the outer layer into the inner layer, the bilayer composite films might show almost the same resistance values of the matrix homopolymers on the electrode. The speculation may be confirmed if we look at the resistance values of the monomer mixture conducting polymer composites.

In the case of the monomer mixture conducting polymer composites, the volume ratio of monomers were varied as follows ; 1ml pyrrole monomer was added to the electrolyte solution system containing 1ml N-methylpyrrole monomer (P1N1 composite), 2ml pyrrole monomer added to the electrolyte solution system containing 1ml N-methylpyrrole monomer (P2N1 composite) and 1ml pyrrole monomer added to the electrolyte solution system containing 2ml N-methylpyrrole monomer (P1N2 composite). The monomer mixture conducting composites showed simply intermediate or additive electric resistance values between those of the two homopolymers ; The resistance value was increased with N-methylpyrrole content. One can expect that certain bonding exists between the two monomers(pyrrole and N-methylpyrrole) with a possible copolymerization.

Table 1 also shows the thermal stability of composites. PPy homopolymer shows higher temperature of initial decomposition(TID) than PNMP homopolymer. This result indicates that PPy has better thermal stability than PNMP. Bilayer conducting polymer films exhibited higher TID's than those of monomer mixture conducting polymer composites regardless of the sequence of the bilayer. The bilayer conducting polymer films showed simple additive thermal stability of the individual polymers. But monomer mixture conducting polymer composites showed slightly different thermal stability and lower TID's being close to or lower than that of PNMP homopolymer as compared with bilayer films, irrespective of the monomer ratios. The thermal stability decreased with increasing N-methylpyrrole contents. It may be assumed that the electropolymeri-

Table 1. The resistance values and thermal stability of samples

Samples	Resistance(Ω)	TID(℃)
PPy homopolymer	25.49	220.78
PNMP homopolymer	912.73	188.32
PNB composite	67.78	205.32
NPB composite	631.25	204.73
P1N1 composite	290.18	186.18
P2N1 composite	45.94	174.68
P1N2 composite	453.75	162.38



—— 5 μm (× 5,000)

Fig. 1. SEM micrographs of PPy/PNMP composites prepared in 0.036M TBADS/ACN solution electrolyte system
(a) PPy (homopolymer) (b) PNMP (homopolymer)
(c) PPy+PNMP bilayer(PNB) (d) PNMP+PPy bilayer(NPB)

zations of monomer mixture conducting polymer composites yield copolymers of pyrrole and N-methylpyrrole monlomers because of their competitive reactivity. It should be noted from Table 1, however, that the PNB composite shows better electric conductivity(i.e. inverse of the resistance value) and good thermal stability than any other composite films, regardless of the preparation methods. The result is due to the inherent superior electric conductivity and thermal stability of PPy to PNMP.

(c)

——— 5 μm (× 5,000)

Fig. 2. SEM micrographs of PPy/PNMP composites prepared in 0.036M TBADS/ACN solution electrolyte system

(a) pyrrole(1) : N-methylpyrrole(1) (P1N1)
(b) pyrrole(2) : N-methylpyrrole(1) (P2N1)
(c) pyrrole(1) : N-methylpyrrole(2) (P1N2)

Figures 1 and 2 show morphological changes of the composites. For the morphological study, we also examined the electrode side of the films. In Figs. 1 and 2, the difference of the electrodeposition reaction of those composites are clearly seen if we compare the morphology of the bilayer conducting polymer films and the monomer mixture conducting polymer composite (P1N1). One can easily see that the tendency of the interpenetration or the reaction between different homopolymers are larger in the case of P1N1 than in the bilayer conducting polymer films having the same polymer contents. The difference in their morphologies may be attributed to the fact that the possibility reactions take place is much larger for the P1N1 than for the bilayer polymer films, since the in-situ formation of the P1N1 starts from the monomer mixture. Even though our results suggest the interpenetration or the reaction between different homopolymers in the bilayer films, the resistance, SEM, and TG measurements give only macroscopic and indirect information on polymer chains. Results of these measurements must be affected not only by bonding and interaction of the polymer chain but also by other unidentified several factors. Thus, further experimental works are now in progress to discuss on the bonding or interaction of the polymer chains based on the more direct evidence on these, such as IR or NMR data.

CONCLUSION

PPy film showed higher conductivity and better thermal stability than PNMP film. In the case of pyrrole/N-methylpyrrole monomer mixture composite films, the resistance value was increased with N-methylpyrrole monomer contents. Bilayer composite films exhibited intermediate resistance values and thermal stabilities between the corresponding homopolymers. It is believed that the PPy/PNMP conducting polymer composite film as well as the monomer mixture composites form copolymers of the two monomer (PPy and PNMP) to a certain extent from SEM, TGA and resistance studies, even though more direct evidence is needed to draw conclusions. It was observed that the PNB bilayer composite films exhibits good electric conductivity and thermal stability as compared with the monomer mixture composite films as well as their corresponding homopolymers.

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