ELECTRICAL PROPERTIES OF P(Py-2FPy)-ZnO COMPOSITE FILMS BY FOUR-POINT PROBE METHOD

Nyunt Win[1], Cho Cho Thet[2] and Ye Chan[3]

Abstract

This work focuses on the investigation of electrical properties of organic-inorganic nanocomposite films. Poly (pyrrole-2formyl pyrrole)-zinc oxide (P(Py-2FPy)-ZnO) composite films are fabricated by ex-situ chemical copolymerization through spin coating technique. Organic copolymer P(Py-2FPy) films were prepared by chemical copolymerization. For the inorganic components, ZnO nanoparticles were synthesized by room temperature solution method. P(Py-2FPy)-ZnO composite films with different concentrations of ZnO nanoparticles are fabricated in order to investigate the effects of ZnO contents on the electrical properties of films. The structural properties of copolymer and composite films were characterized by Ultraviolet-visible (UV-Vis) spectroscopy. The electrical properties of composite films including the sheet resistivity and conductivities of the composite films are measured by four-point probe method. Finally, the results of sheet resistivity and conductivity of composite films depending on concentration of ZnO nanoparticles are discussed. It was found out that the conductivities of composite films were increased with increasing the concentration of ZnO nanoparticles.

Keywords: copolymer, chemical polymerization, composite films, sheet resistivity, conductivity, *ex-situ*, spin coating.

Introduction

Metals are of great interest in industry as structural materials due to their high density and high strength to weight ratio. Some applications are limited due to their poor corrosion resistance. Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Anti-corrosion coatings protect metal components against degradation due to moisture, salt spray, oxidation, or exposure to a variety of environmental or industrial chemicals in a range of industries. Metal anticorrosion inhibits corrosion through physical and chemical effects which are great significance for industrial production and biomedical materials. The development of industry and science and technology such as metal chemistry, alloying effects, and the electrochemical and polymer field are improved the corrosion resistance of metals.

Coatings used for corrosion protection are mainly of three types such as metallic, organic and inorganic. The application organic coating establishes a barrier between substrate material and environment. It includes protected materials for paints, varnishes and lacquers, water-emulsion and solution finishes, organosols and plastisols. Organic corrosion inhibitors can be used alone or in combination with inorganic corrosion inhibitors for enhancing the anti-corrosive properties of a coating. Coating technology is a very common method which includes sol-gel coatings (Irina Stambolova et al., 2018), electroless coating (Fayomi *et al.,* 2019), electrochemical coating (Wenzheng Lu et al., 2020) and thermal and plasma-enhanced atomic layer deposition (Min Li *et al.,* 2019) and chemical oxidation (De Cheng *et al.,* 2021). Anticorrosive coating materials include organic polymers (ChandrabhanVerma *et al.,* 2020), metal oxide (Kalendova *et al.,* 2009) and graphene-containing composites (Hongran Zhao *et al.,* 2021).

From the observation of new fabrication strategies of organic-inorganic composite films, nanocomposites are derived from organic polymers and inorganic nanoparticles. The composites are expected to display synergistically improve the electrical properties of composite films by

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combining the attractive functionalities of both components. Therefore, polymer-based inorganic nanoparticle composite films will be interesting in several applications as new conductive polymeric materials. In addition, organic polymers are considered to be good hosting matrices for composite materials since they can easily be tailored to yield a variety of bulk physical properties.

Inorganic nanoparticles (TiO_2 and ZnO) possess outstanding optical, catalytic, electronic and magnetic properties which are significantly different from their bulk states. The polymer inorganic composites comprise inorganic nanoparticles like TiO2 or ZnO are uniformly dispersed in and fixed to a polymer matrix. The interfacial surface area of composite was increased due to higher surface area of nanoparticles. Besides, smaller particle size allows a much more homogeneous distribution of a composite material. In the integration of inorganic components in polymer matrix, the important criteria are (i) suitable synthetic method of inorganic nanoparticles in order to well dissolve in monomer solutions (ii) the enough stirring time is necessary for the homogeneous composite solution (iii) preparation technique of composite film formation. In this case, it is very important to consider the polymerization methods which are uncomplicated and the possibility of film formation.

In this work, inorganic ZnO nanoparticles in organic Py-2FPy copolymer were composited (Nyunt Win et al., 2020). The composite P(Py-2FPy)-ZnO film was prepared in order to study the electrical properties of films. The conductivities of composite films depending on various concentrations of inorganic ZnO are investigated by using four-point probe measurement. This work aims to investigate the enhancement of electrical conductivity from the development of organic-inorganic composite films.

Experimental Details

Preparation of the Organic Monomer Solution

(200 mg, 3 mmol) of Py and (286 mg, 3 mmol) of 2FPy were mixed and dissolved in 2 ml of chloroform ($CHCl_3$). They were stirred at the room temperature for 30 min to obtain the monomer solution (Yusuke Hoshina and Takaomi Kobayashi, 2012).

Preparation of the Inorganic ZnO Nanoparticles

ZnO nanoparticles were synthesized by room temperature solution method. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and ethanolamine ($NH_2CH_2CH_2OH$) and 2-methoxyethanol were used as a starting precursor, a solution stabilizer and a solvent. 1 g of $Zn(CH_3COO)_2.2H_2O$ and 0.28 g of ethanolamine in 10 mL of 2-methoxyethanol were vigorously stirring for 12 h for the hydrolysis reaction in air (Sun Y. et al., 2011).

Preparation of the Composite Films

486 mg of as-synthesized ZnO solution was added to 486 mg of monomer solution. Thus, the weight ratio of inorganic to organic is 1:1. The mixture was continuously stirred for 24 h. Then, the solution containing (995 µl, 13 mmol) trifluoroacetic acid (TFA) and (2 ml) $CHCl_3$ was additionally put to composite solution at room temperature. After that, the mixed solution was spin-coated onto the Petri dish at 20 rpm using a home-made spin coater until to complete the formation of copolymerization. After that, the film was successively washed by excess deionized water and acetone and dried in a vacuum oven for 12 h. Figure 1 illustrates the synthesis route scheme of the composite films.

Characterization Tools

The UV-Vis spectroscopy was performed in order to examine the absorbance values of all synthesized samples. The UV-Vis spectra were obtained by using the Shimadzu UV-1800 UV-Vis spectrophotometer. The electrical properties were measured by Keithley 2450 source meter.

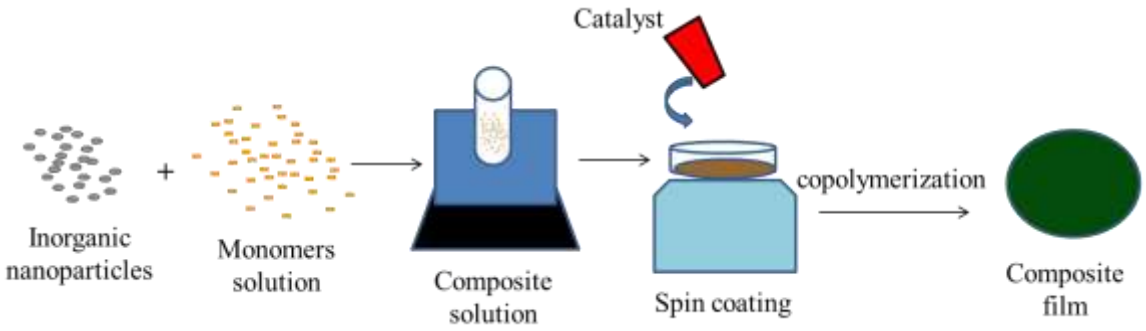

Figure 1 Schematic of *ex-situ* synthesis inorganic-organic nanocomposites films

Results and Discussion

Figure 2 shows the comparative UV-Vis spectra of ZnO, copolymer film and P(Py-2FPy)-ZnO composite films respectively. The optical absorption wavelengths of monomers, 2FPy and PPy, are found at 266 and 305 nm. However, the new copolymerization peak is formed at the wavelength 454 nm after the TFA catalyst is added. This peak indicated that the 2FPy group is incorporated into the chemical structure of the conjugated polymer chains (Yusuke and Kobayashi, 2012). When ZnO is present in the copolymer matrix of composite film, the absorption intensity of polymer chains is greatly increased. Besides, the weaker band is additionally appeared around 680 nm. This is due to strong interaction of ZnO with pyrrole segments to form bipolaron state which can enhance the electrical conductivity of composite films than pure copolymer film. The movement of polarons and bipolarons along the polymer backbone gives rise to enhanced conductivity of polymer film (Bredas and Street, 1985).

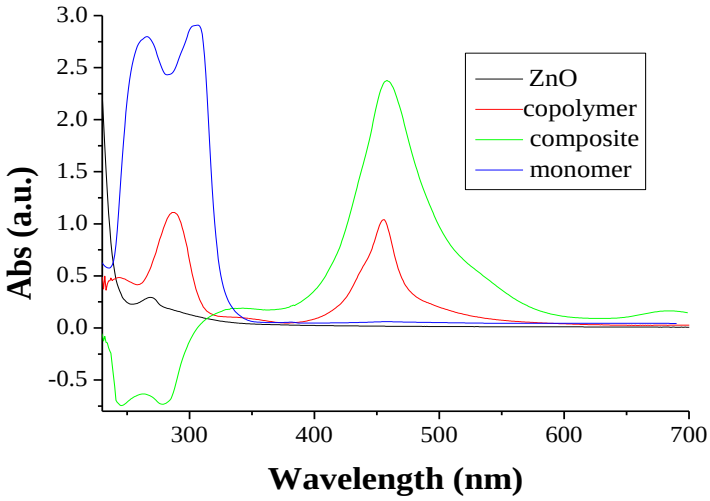

Figure 2 UV-Vis absorption spectra of ZnO, monomer, copolymer film and P(Py-2FPy)-ZnO composite films

Table 1shows the experimental parameters of films depending on concentration of ZnO nanoparticles obtained from the four-point probe measurement.

The sheet resistivity (ρ) of the conductive films is calculated by using the following formula:

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$$\rho = \frac{\pi}{\ln 2} \times \frac{V}{I} \times t \qquad (1)$$

where, V is voltage between the inner two probes of meter, I is current, t is the thickness of the films. Finally, the conductivity (σ) is determined by using the relationship:

$$\sigma = \frac{1}{\rho} \qquad (2)$$

Figure 3(a) and (b) illustrate the graph of sheet resistivity of pure copolymer and composite films depending on different volume of ZnO nanoparticles. As shown in these graphs, sheet resistivity of the films is decreased with increasing the volume of ZnO nanoparticles. It was found out that the values of sheet resistivity for all composite films were decreased and their conductivities were increased than pure copolymer films. The conductivity of the pure copolymer (0 mL of ZnO nanoparticles) films showed the lowest while the conductivities of composite films were enhanced with the increasing volume of ZnO. It is remarkable to note that the highest conductivity is obtained for the films composited with 0.5 mL of ZnO nanoparticles within the investigated volume limits of ZnO. This improvement of conductivity may be due to the facts that copolymers are associated with the structure of the P(Py-2FPy) and the metal oxide nanoparticles was incorporated into the polymer backbone with ionic complex formation as the dopant (Bredas and Street, 1985). Figure 4 shows comparison of decreasing sheet resistivity and increasing conductivities of pure copolymer (zero mL volume of ZnO nanoparticles) and composite films (0.1 to 0.5 mL of ZnO nanoparticles composited with copolymer solution).

Table 1 Experimental parameters of the films depending on concentration of ZnO nanoparticles

Concentration of ZnO nanoparticles (mL)	Thickness (t) ($\times 10^{-1}$ cm)	Voltage (V) (mV)	Current (I) (μA)	Sheet Resistivity (ρ) ($\times 10^{4}$ Ω-cm)	Conductivity (σ) ($\times 10^{-4}$ Scm^{-1})
0	0.0344	5.5869	0.0020	4.3550	0.2296
0.1	0.047	10.1503	0.01219	1.7736	0.5638
0.2	0.1625	0.051	0.0009	0.4173	2.3962
0.3	0.05	17.5038	0.1071	0.3703	2.7001
0.4	0.0538	0.6424	0.004942	0.3169	3.1552
0.5	0.0919	0.0053	0.000226	0.0977	10.2000

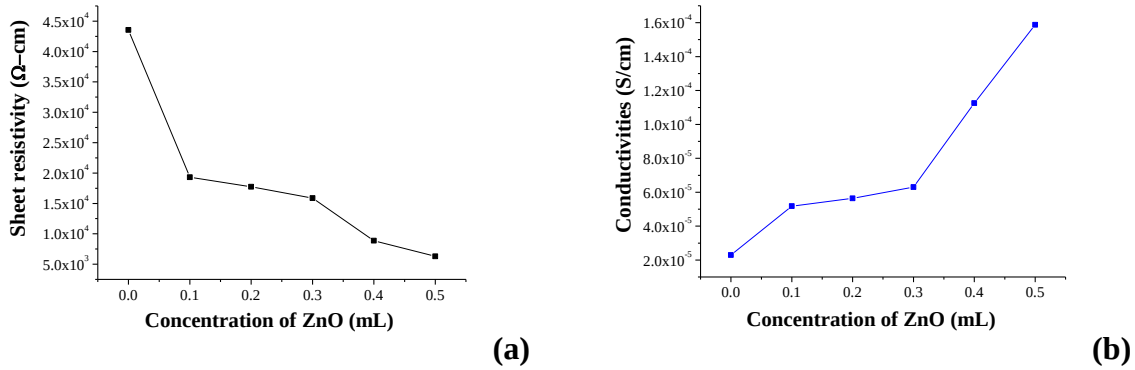

Figure 3 (a) Sheet resistivity and (b) conductivities of P(Py-2FPy)-ZnO composite films depending on concentration of ZnO nanoparticles

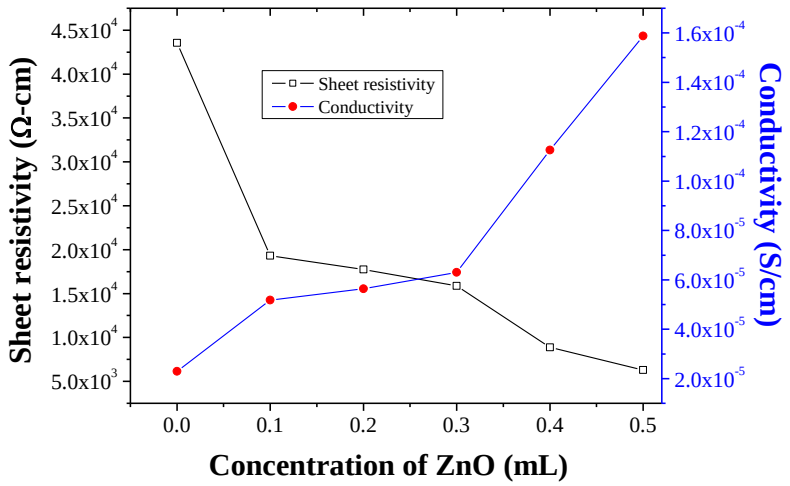

Figure 4 Sheet resistivity and conductivities of P(Py-2FPy)-ZnO composite films

Conclusions

The electrical properties of composite films depending on effects of inorganic ZnO nanoparticles in the organic matrices (copolymer) are systematically investigated by four point-probe method. It is found out that the values of sheet resistivity of the composite films are decreased and their conductivities are increased with increasing concentration of ZnO nanoparticles. This may be due to increasing concentration of charge carriers which tends to increase in doping of metal oxide nanoparticles in the copolymer backbone. This can be also explained that the delocalization effect which is associated with the doping process and that produces polarons and/or bipolarons in the composite structure which in turn enhance the conductivity. Therefore, all these results are directed to promote the conductivities of composite films for their potential applications for anticorrosion technology.In conclusion, by exploiting the physics of the inorganic nanoparticles, organic polymer and polymeric nanocomposites, a new functional composites P(Py-2FPy)-ZnO materials will lead to important coating materials due to their electrical conductivity and mechanical flexibility by the unique combination of inorganic and organic materials.

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