ELECTRICAL PROPERTIES OF REDUCED GRAPHENE OXIDE-CONDUCTIVE COPOLYMER COMPOSITE FILMS*

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Abstract

Conductive composites include any composite having significant electrical conductivity. An electrically conductive filler such as carbon-based materials like graphene when added to insufficient quantities of a polymeric resin, a conductive composite is formed. This research focus on the preparation of the conductive polymer using the organic copolymer and the inorganic particles. Copolymer P(Py-co-FPy) films were prepared by chemical copolymerization of pyrrole (Py) and pyrrole -2carboxaldehyde (FPy) in the trifluoroacetic acid (TFA) catalyst and chloroform ($CHCl_3$) solvent. As the inorganic component, reduced graphene oxide (rGO) was synthesized by chemical reduction method. In preparation of P(Py-co-FPy)-rGO composite films the different grams of rGO powders are incorporated into the copolymer matrices by ex-situ chemical copolymerization through spin coating technique. The structural and electrical properties of copolymer and composite films were characterized by Fourier transform infrared spectroscopy (FTIR) and the conductivities of the composite films are increased with the concentration of inorganic particles. It is found that the conductivities of P(Py-co-FPy)-rGO (0.3 g) composite film are greater than those of pure copolymer P(Py-co-FPy) film.

Keywords: copolymer, composite film, conductivity, four probe method, rGO, sheet resistivity

Introduction

Recently, lightweight conductive composite materials with high electrical conductivity have been focused in many applications including battery components, electrodes, electromagnetic interference shields and circuitry components. Conductive composites include any composite having significant electrical conductivity. The conductivity of the composites depends on the filler contents. The electrical conductivity of the composites can be changed by several orders of magnitude by small variation of the filler content (Qu et al., 2018). Thus, the conductivity of the composites can be controlled by varying the volume fraction of the conductive filler for the various applications. The values of electrical conductivity of polymers are between 10-14 and 10-17 Scm-1. The composite materials must have an electrical conductivity in the range between 10-12 and 10-2 Scm-1 for the conductive applications (Alemour et al., 2019).

The electrical conductivity of conductive composites depends on filler type, shape, size, and filler dispersion and distribution in the composite. The conductive filler type has an important effect on the electrical conductivity of the composite. Carbon based materials such as graphite and graphene can be used as conductive filler (Mohammad et al., 2022; Kumar et al., 2017). In addition, the electrical conductivity of each material is different and thus, the electrical conductivity of the composite will be different depending on each filler type used.

Conducting polymers (CPs) are regarded as promising pseudo-capacitive materials because of their large specific capacitance and the characterization of many active sites. Most commonly used polymers are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and poly 3,4-ethyl-enedioxythiophene (PEDOT). Besides, various doping types of conducting polymers are used in supercapacitor as electrode materials. The lifecycles CPs are shorter than those of carbon-based materials. Conducting polymers are significant electrode materials for pseudocapacitors due to their high capacity, improved conductivity, ease of synthesis, and low

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cost. These polymers are often composited with other materials such as carbon nanotubes or metal oxides in order to further enhance their electrochemical properties. This hybrid approach can improve the overall performance of supercapacitors, including their capacitance, cycle life, and energy density. The materials for electrolyte and electrode are crucial in supercapacitors.

Carbon-based electrode materials are frequently used in supercapacitors because of high surface area, good electrical conductivity, chemical stability, versatility and costeffectiveness. These properties are contributed to the high-power density, long cycle life and overall efficiency of supercapacitors. Among the carbon derivatives materials for supercapacitors, reduced graphene oxide (rGO) has garnered considerable interest due to its superior properties including strong mechanical stability, superior electrical conductivity, and large surface area. rGO is a suitable surface area compared to graphene oxide (GO) since it can enhance its ability to store charge which in turn improve the capacitance and overall performance of supercapacitors. rGO generally shows better electrochemical stability, making it more reliable for long-term applications in energy storage devices. In this work, the electrical properties of reduced graphene oxide composited with copolymer film is investigated by four probe method for the application of supercapacitors.

Experimental Details

Preparation of P (Py-co-FPy) Copolymer Films

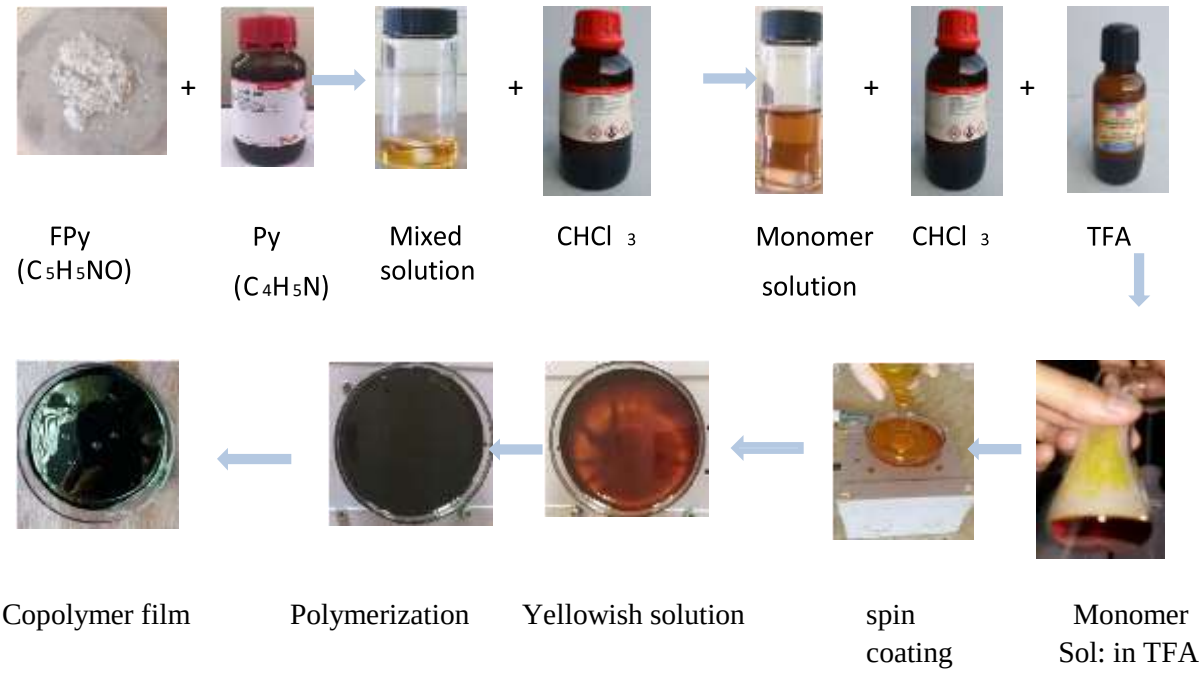

Figure 1 Preparation of P (Py-co-FPy) copolymer film

Copolymer solution is prepared by 207 μL of pyrrole (C4H5N) and 286 mg of pyrrole2-carboxaldehyde (C5H5NO) in 2 mL of chloroform (CHCl3) (Hoshina and Kobayashi, 2012). Then, they were stirred at the room temperature (RT) for 1h in order to form homogeneous monomer brown solution. Then, the mixture containing of 2 mL of CHCl3 and 1 mL of trifluoroacetic acid (TFA) are added to the monomer solution. As a result, the color of the solvent immediately changes from transparent brown to yellowish red. Then, the mixed solution is spin-coated onto the 9 cm diameter of the Petri dish at 25 rpm by using a homemade spin coater. The spin coating process is carried out for 2:30 h at room temperature to be completed polymerization process. Finally, a metallic greenish copolymer film was casted into 11 the Petri dish as shown in

Figure 1. After that, the film was washed by distilled water until all residuals of reaction in the film is completely removed. Then, the film was washed again with acetone and dried in a vacuum desiccator for 24 h. This film was chemically doped by iodine (I2) by before FTIR and four probe measurements.

Preparation of P (Py-co-FPy) – rGO Conductive Composite Films

Composite films were prepared by ex-situ polymerization method. Firstly, different weight of rGO powders including 0.1, 0.15, 0.2, 0.3 g were mixed with the monomer solution. The mixture solution was stirred for several days until to become the well dissolved solution. Then, the mixed solvent of 2 mL CHCl3 and 1 mL TFA are added to the homogeneous solution. Then, the solutions were spin-coated onto the Petri dishes. After that, the films were washed by distilled water until all residuals of reaction in the film is completely removed. Then, the films were washed again with acetone and dried in a vacuum desiccator for 24 h. Finally, composite films were successfully obtained as presented in Figure 2. All films were doped by iodine (I2) before four probe measurement.

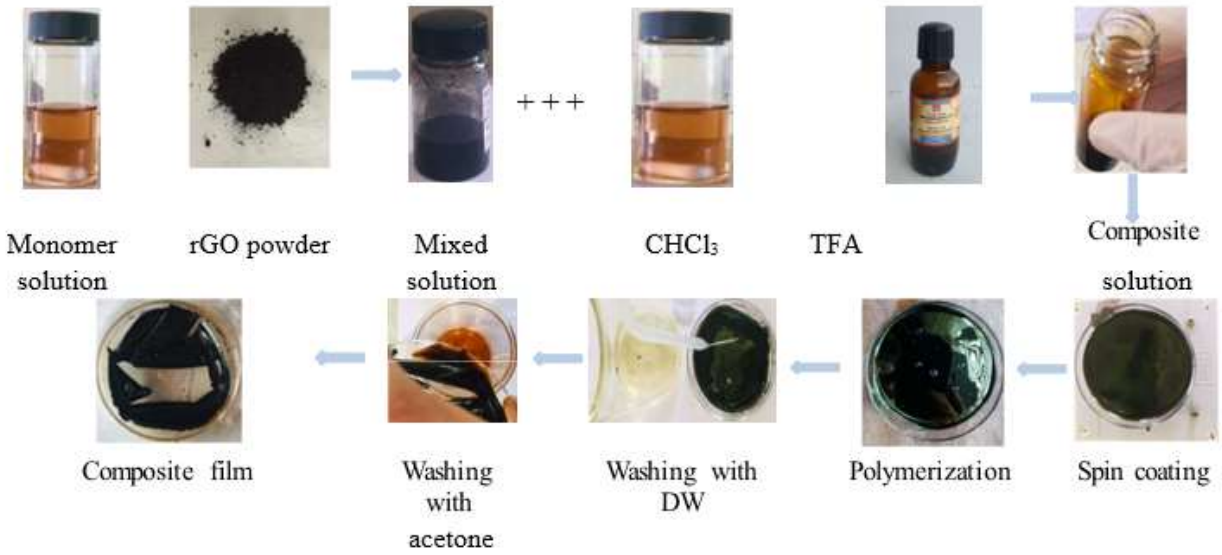

Figure 2 Preparation of composite film

Results and Discussion

FTIR analysis is carried in order to study the compound identification of pure and composite films. FTIR spectra of the films before and after iodine doped are shown in Figure 3. Before I2 doping, the peaks at 3361.88, 3384.27, 3366.68, 3380.28, 3398.67 cm-1 are due to the O-H stretching vibration. The peak of C = N stretching is occurred at 1658.64, 1653.84, 1645.05, 1655.44, 1661.04 cm-1 respectively. The peak for C-F bond at 1476.95, 1487.33, 1477.13, 1481.77 cm-1. The peaks at 799.82, 710.26, 789.43, 792.63, 797.42 cm-1 are C-H bonding. The peaks at 1174.06,1176.45, 1180.45, 1177.25, 1176.45 cm-1 are related to the C-O stretching of amine group. After I2 doping, the peaks observed at 3341.09, 3343.49, 12 3359.48 cm-1 are assigned to O-H stretching vibration. The peaks of C=C stretching at found at 1661.04 cm-1and the absorption bands at1587.47, 1595.47 cm-1 are vibration mode of the N-H bending (Yang et al., 2007). The peaks at 794.22, 697.47, 797.42 cm-1 are aromatic C=C bending. The peaks at 1121.28, 1128.48, 1134.87 cm-1 can be related to C-O stretching (Factors, I.R.). One more additional peak within 600 – 480 cm−1 regions are due to the presence of iodine which is corresponded to aliphatic C–I stretch. Thus, iodine atoms are incorporated into backbone of

copolymers.

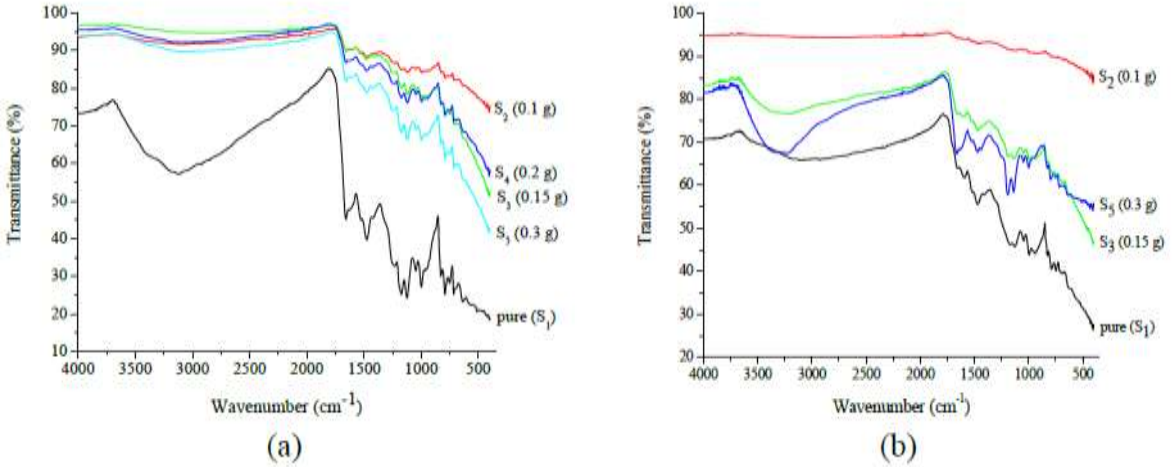

Figure 3 FTIR spectra of films (a) before and (b) after iodine doping

Figure 5 shows the structure of the composite film was further studied by X-ray diffraction (XRD). In the case of rGO an intense broad peaks at 24.64˚and 26.40˚which are very close to reduced graphene oxide's peak and its interlayer distance were 0.36 Å and 0.34 Å. The XRD pattern of copolymer shows figure diffraction peaks extending around 15 - 24˚. The diffraction peak of the composite, the diffraction pattern of rGO with 2θ = 26.50˚. The peak confirm the presence of rGO in the composite. On the other hand, the peak 2θ = 20.7˚confirm the presence of polymer (Bejjanki and Puttapati,2023).

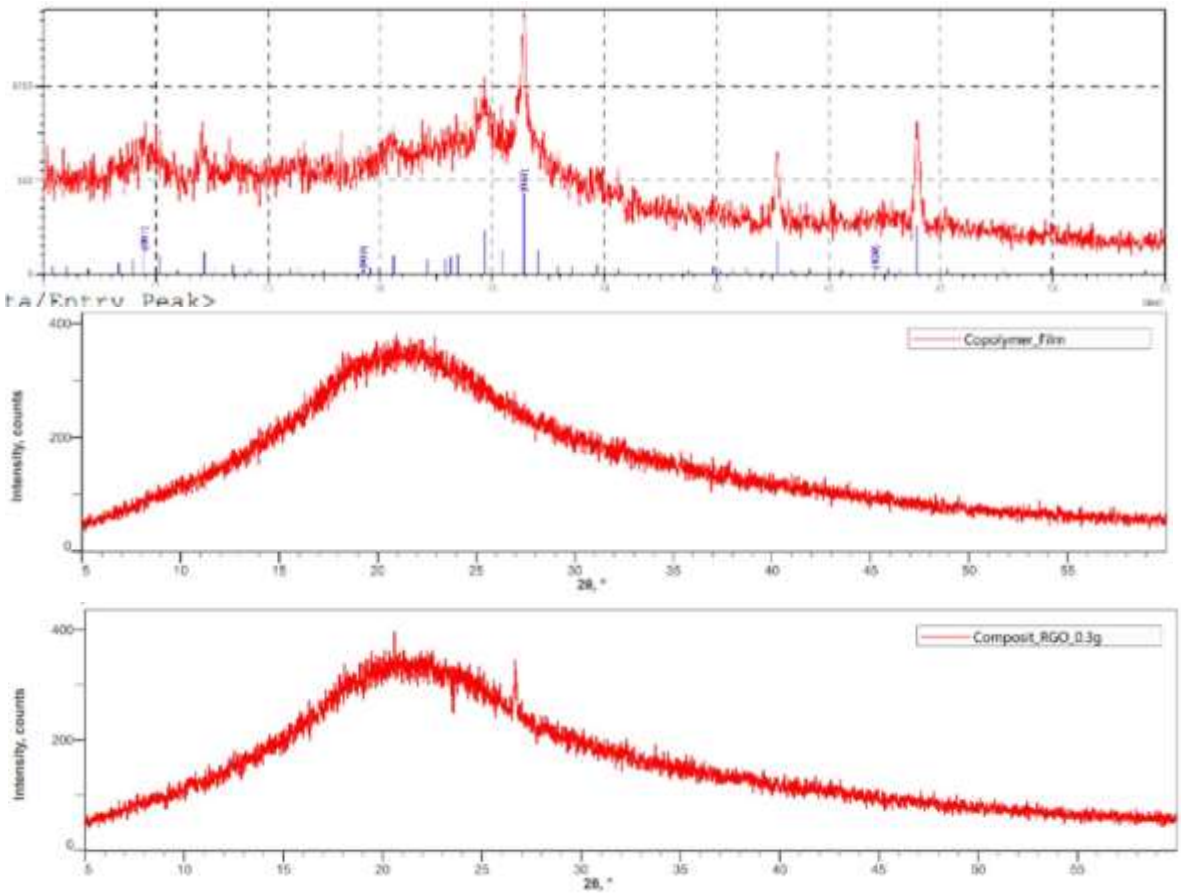

Figure 4. (a) XRD spectrum of rGO powder, XRD spectra of films (b) pure copolymer film and (c) composite film

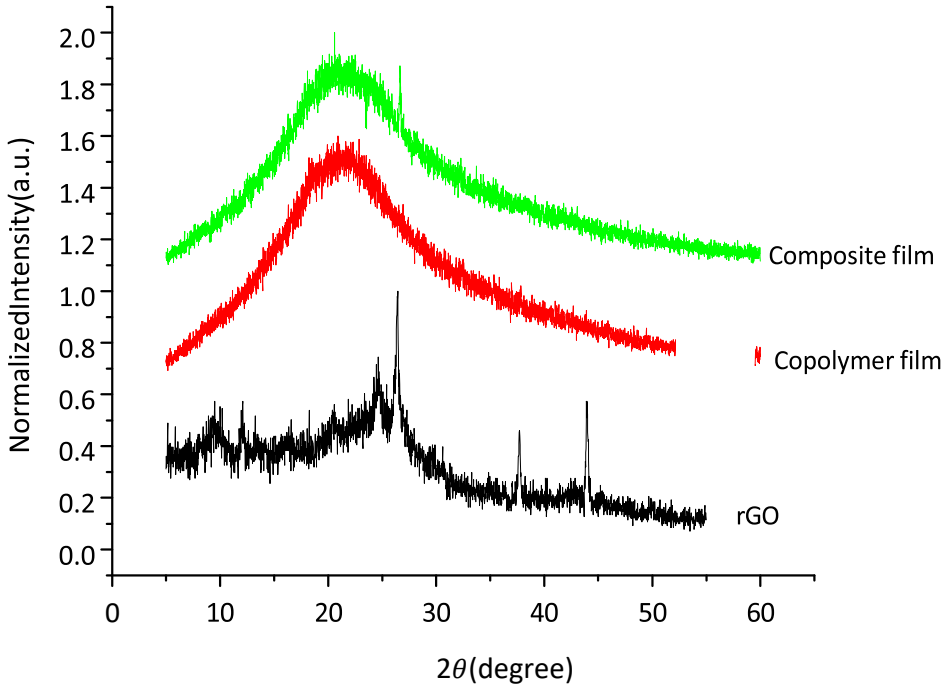

Figure 5. XRD spectra of the films

Figure 6 shows the graph of sheet resistivity and electrical conductivities of the films depending on different of rGO content (0.1 g, 0.15 g, 0.2 g, 0.3 g). The conductivity of the pure copolymer showed the lowest value. It was found out that the highest conductivity was obtained for the films composited with 0.3 g of rGO powder among the four samples. As shown in the graph, the conductivities of the films were increased with an increasing weight of rGO powder. The increase in electrical conductivity with the increasing concentration of rGO are due to the combination rGO in the copolymer matrix which gives rises to the conduction of charge carriers. The enhancement in concentration of charge carriers are tended to increase the doping of rGO in copolymer backbone. This can be explained that the delocalization effect which is associated with doping process and that produces polarons and /or bipolaron in the composite structure which in turn enhance the conductivity. Table 1 shows the values of sheet resistivity and conductivities of pure and composite films at different rGO content. The compared graph between sheet resistivity and conductivity is illustrated in Figure 7.

Table 1. Sheet resistivity and conductivities of pure copolymer and P(Py-co-FPy)-rGO composite films

Sample	rGO content (g)	Thickness (d) (mm)	V/I	Sheet resistivity (ρ) (kΩ cm)	Conductivity (σ) (Scm^{-1})
S1	0	1.73	7936663	1.522	0.657×10^{-3}
S2	0.1	1.32	3541418	0.872	1.147×10^{-3}
S3	0.15	0.30	472909	0.715	1.399×10^{-3}
S4	0.2	0.11	1347376	0.619	1.616×10^{-3}
S5	0.3	0.55	94593	0.262	3.817×10^{-3}

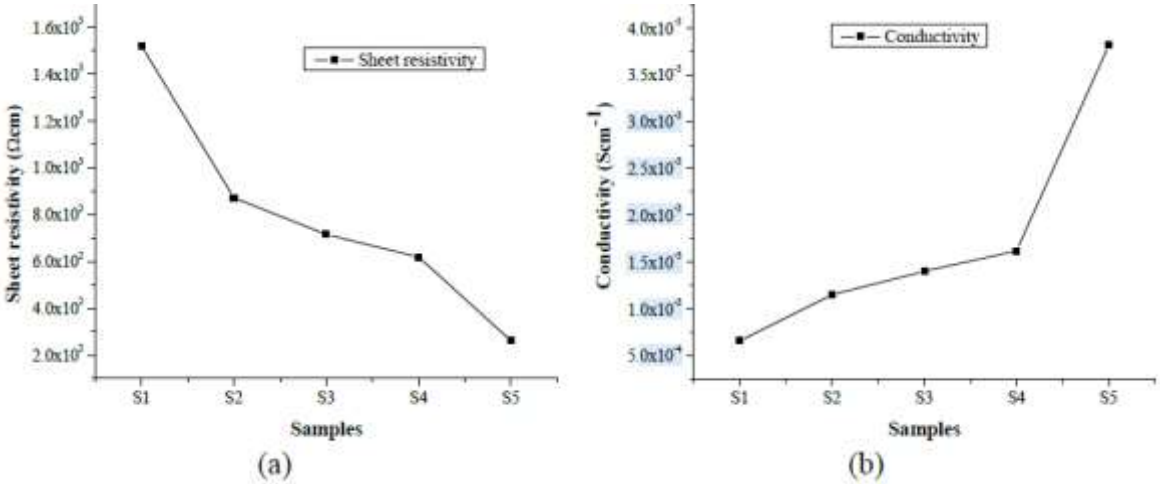

Figure 6 Graph of (a) sheet resistivity and (b) electrical conductivity of the films depending on different gram of rGO

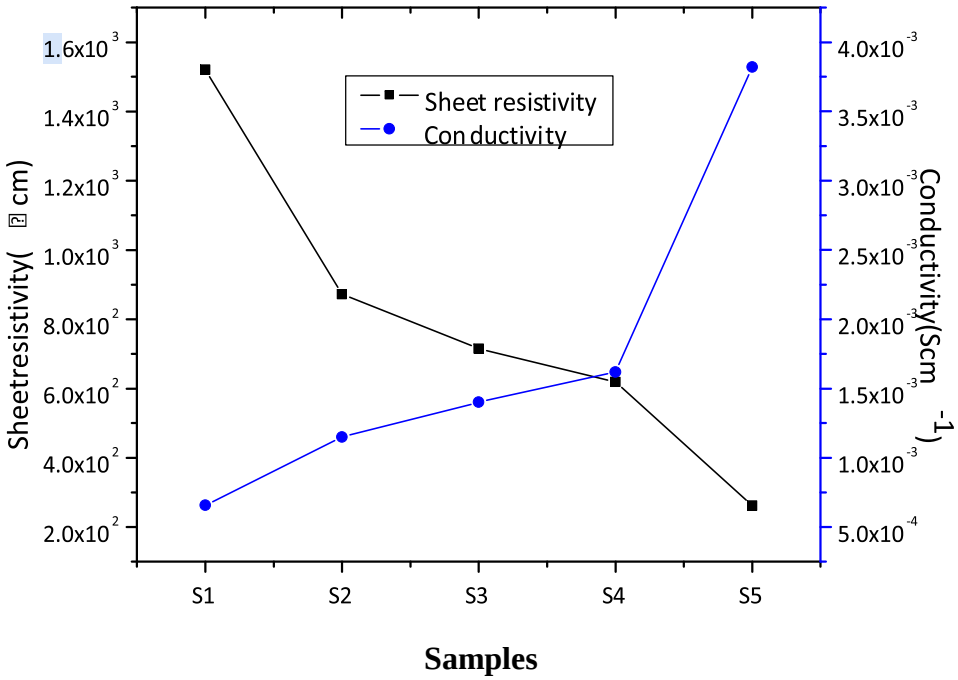

Figure 7. Compared graph of sheet resistances and conductivities of pure copolymer and composite films

Conclusions

In summary, the conductive copolymer film and composite films are prepared by exsitu chemical copolymerization process through spin coating method. The DC electrical properties of copolymer (PPy-2FPy) and composite films P (Py-co-FPy)-rGO are systemically investigated by four probe method. It is found out that the values of conductivity of the composite films are enhanced with increasing concentration of inorganic rGO particles. Besides, it is remarkable to note that the conductivities of P (Py-co-FPy)-rGO (0.3 g) composite film is higher than P (Py-co-FPy)-rGO (0.1, 0.15, and 0.2 g) composite films within the investigation rGO content. FTIR spectra of film proved that formation of conjugated chemical structure is in their copolymer film. It means that, rGO particles combined very well in the copolymer matrix in order to integrate the

composite film and performed in the enhancing of charge carriers which in turn improve the electrical conductivities of composite films. Therefore, the research finding can be used in conductive applications such as electrostatic dissipation and shielding.

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