

*Full Length Research Paper*

# Synthesis and characterization on electrical properties of conducting polymer of polypyrrole and polypyrrole/cadmium sulfide composites

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**A series of conducting polymer polypyrrole (PPy) and polypyrrole/cadmium sulfide (PPy/CdS) composites were successfully synthesized using the chemical reaction method. PPy/CdS composites were prepared with CdS concentration percentages ranging from 2 to 10%. From the X-ray diffraction (XRD) results, the XRD pattern showed evidence of conducting structure of polymer PPy and PPy/CdS composites. The spectrum clearly indicated that PPy polymer was amorphous. From the PPy/CdS composites spectrum, the six major peaks that were observed for all the samples were well known peaks that originated from CdS. From the results obtained, it shows that the conductivity of conducting polymer PPy and PPy/CdS composites at the low temperature range increased with the increase in percentage of CdS. The electrical conductivity increased from  $2.85 \times 10^{-7}$  to  $1.66 \times 10^{-5}$  S/cm in the low temperature range of 100 to 300K. While for the PPy/CdS composites, the increase of conductivity showed the same trend with the low temperature studied where the values increase from  $2.11 \times 10^{-5}$  to  $8.74 \times 10^{-5}$  S/cm.**

**Key words:** Conducting polymer, polypyrrole, polypyrrole/cadmium sulfide composites, electrical Conductivity.

## INTRODUCTION

Polymers were generally considered to be electrically non-conducting. However, scientists have discovered that certain classes of polymers called conjugated polymers, which contain many double bonds in their structure, are actually semi-conductors with unusual electrical properties.

Numerous studies have been performed on the conjugated polymers, such as polypyrrole, polyaniline, polythiophene and polyphenylene, since the discovery of the conducting properties of polypyrrole in 1979. Pohl and coworkers were the first to synthesize and characterize semiconducting properties in conducting polymer back in the 1960s (Stenger-Smith and John 1998). The most widely studied conducting polymers include polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh). Among them, PPy has attracted

much attention owing to its unique electrical conductivity, redox property, excellent environment stability, as well as the virtue of easy preparation by both chemical and electrochemical approaches in various organic solvents and in aqueous solution (Li et al., 2009).

The preparation of electrical-conducting CdS-polymer (poly(acrylonitrile), poly(vinylidene fluoride), etc.) composites using the organosols of CdS was investigated by Takakazu et al. (1986). Some of the composites have relatively high electrical conductivity and seem to have practical use in making electrical devices (Yunos et al., 2011). Lim et al. (2007) studied the preparation and characterization of conducting polymer polypyrrole and polyethylene glycol composite films. The conductivity of the composite films prepared from using 0.2% poly(ethylene glycol) (PEG) was found to exhibit the highest conductivity among all the prepared composite films measured at room temperature. They attributed this to the increase of conjugation chain length with the increase in PEG percentage.

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The work to improve the conductivity of PPy by doping or chemical modifying has been made with great progress. In order to get a conducting polymer material suitable for applications, it has to overcome certain limitations, such as poor mechanical properties and processibility, and instability in ambient conditions. Several approaches have been made by many researchers to improve these properties and one of the best ways is the formation of conducting composites.

In this paper, we reported our work on preparing conducting polymer PPy and PPy/CdS composites via chemical reaction method to study the electrical properties for both of the materials. Structured element is the most important factor to determine the morphological characteristics of the composites material. Therefore, X-ray diffraction (XRD) techniques were used to characterize the structure of the PPy and PPy/CdS compounds. On the other hand, electrical properties of the PPy and PPy/CdS were characterized using four-point probe techniques.

## EXPERIMENTALS

The conducting polymer, PPy/CdS composite compound powder was synthesized by traditional chemical reaction method. First of all, pyrrole monomer was distilled and stored at 4°C before used. All other reagents were used without further purification, including iron (III) chloride 6-hydrate, FeCl<sub>3</sub>, cadmium sulfide and CdS. Synthesis of PPy/CdS composites were carried out under several CdS percentages. The composite powders were synthesized with 2, 4, 6, 8 and 10% of CdS in the pyrrole solution with 6 h stirring after the powders were mixed at definite molar ratio. The concentration of PPy was fixed at 0.2 M and also FeCl<sub>3</sub> at 0.2 M. The solutions were filtered, and then were washed thoroughly with distilled water and the filtration yields were dried in a conventional oven for 24 h. After undergoing the drying process, the powders were compressed into pellets using manual hydraulic press for further measurement.

The crystal structure of the powders were characterized by X'Pert Pro model PW 3040 Philips X-ray diffractometer using Cu-K $\alpha$  radiation operated on working voltage at 40 kV and acceleration current at 100 mA. For powder sample, XRD profile was collected with an angular range of 2 $\theta$  from 20 to 80° in steps of 0.1° with a counting time of 2 s and the wavelength of X-ray 1.54 Å was used. X'Pert HighScore Plus software was used for the qualitative phase analysis of the samples. The electrical conductivity was measured at low temperature using standard four point probe technique. Investigation of the electrical conductivity of the PPy/CdS composites has been investigated using standard four-point probe method at low temperature, ranged from 100 to 300K and the thickness of the samples was determined by using digital calipers. A Keithley 2400 Source Meter was used as a constant current source, while the voltage was measured with a Keithley 2700 Multimeter/Data Acquisition System.

## RESULTS AND DISCUSSION

XRD techniques was used to identify the crystalline Phase of the synthesized conducting polymer PPy

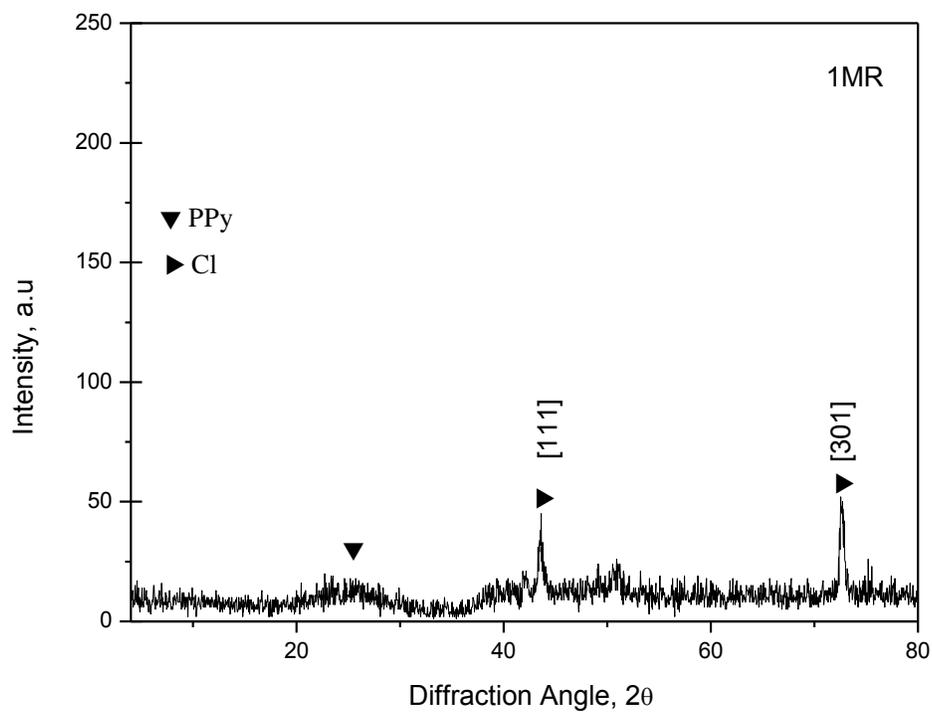
and PPy/CdS composite. Figure 1 shows the XRD patterns for conducting polymer polypyrrole doped with concentration of 0.2 M iron (III) chloride 6-hydrate (FeCl<sub>3</sub>) in solution containing 0.2 M pyrrole. It was clearly revealed that the sample is amorphous in nature from 20 to 30°. The first broad amorphous centered at 2 $\theta$  = 23.46° for 1 molar ratio (MR) is a typical hump for conducting polymer polypyrrole. This is in agreement with earlier studies on PPy (Cheah et al., 1999; Visy et al., 2005). The other two peaks centered at around 2 $\theta$  = 43 to 44° and 2 $\theta$  = 71 to 72° for each molar ratio are identified to belong to chlorine atoms (Cl atoms). These two peaks at 2 $\theta$  = 43 and 71° corresponding to d-spacing values of 2.079 and 1.301 Å are observed and attributed to the (111) and (301) planes, respectively.

These peaks are the result of a redox mechanism from polymerization process (Visy et al., 2005) according to reaction. Moreover, these two peaks confirmed the formation of polarons as generally known after polymerization process of PPy, where Cl ion was attracted to a functional group of PPy (Parker 2002) forming a single polaron during the polymerization process (Benseddik et al., 1995).

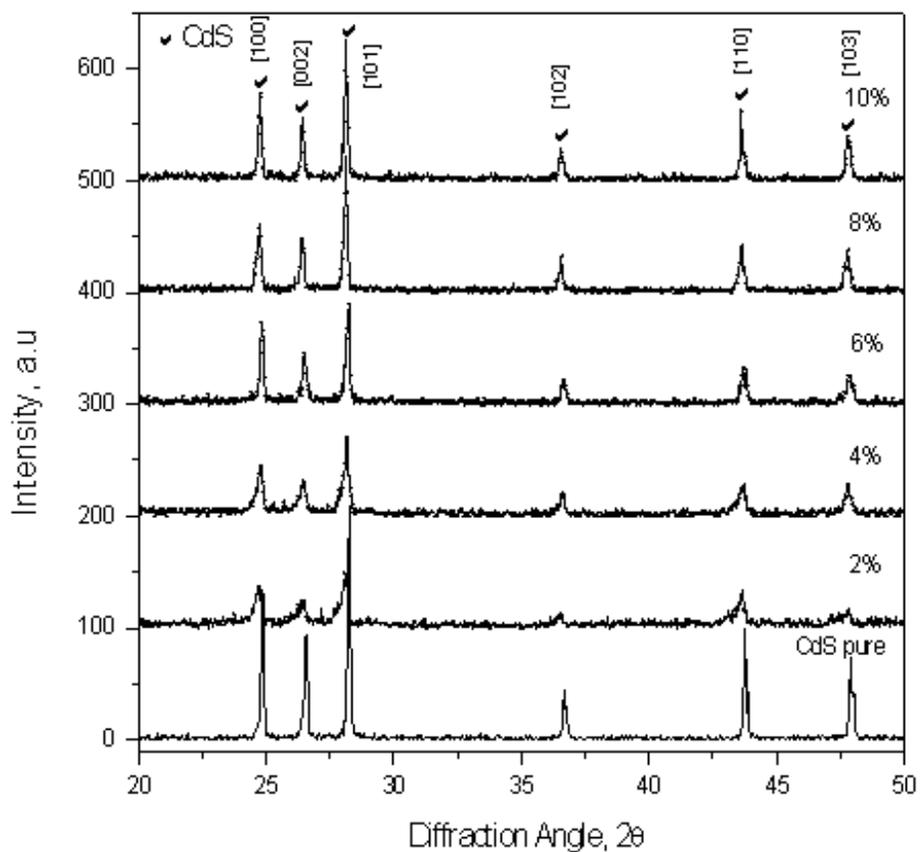
Here, we can see that the six major peaks that were observed for all the samples are well known peak that originated from CdS. The peaks centered at 2 $\theta$  = 24, 26, 28, 36, 43 and 47° corresponding to d-spacing values of 3.58, 3.36, 3.16, 2.45, 2.07 and 1.90 Å are observed and attribute to (100), (002), (101), (102), (110) and (103) planes, respectively. From the patterns obtained, the diffraction peaks at 2 $\theta$  = 24, 26 and 28° which belongs to CdS overlapped with the broad hump from the conducting polymer PPy is as shown in Figure 1. The 6 peaks for pure CdS were present in the spectra of all doped PPy/CdS composite (Figure 2). The peaks intensity gradually increased with increase in CdS percentages. The observed d-spacing values with its standard data (ICSD 01-075-1545) are tabulated as shown in Table 1.

The XRD pattern shows the evidence of the influence of the different concentration of the inorganic particles, CdS and the dopant (oxidant) that was used to prepare the PPy/CdS composite on the structure of conducting polymer PPy and PPy/CdS composites. Previous studies indicated that the crystallinity of composites containing PPy doped with various dopants was enhanced with the addition of the dopant (Allen et al., 1997; Cheah et al., 1998).

The conductivity of compressed pellets of PPy and PPy/CdS powders was studied using four-probe method. The pellets of samples obtained for 1 MR were used for conductivity studies. The results show that the conductivity increases with increase in dopant concentrations and with increasing temperature. Figure 3 displays the dependence of the direct current (DC) conductivity of conducting polymer PPy with 1 M. The electrical conductivity increased from 2.85 × 10<sup>-7</sup> to 1.66



**Figure 1.** X-ray diffraction pattern of conducting polymer (PPy) with 1 molar ratio (1 MR).



**Figure 2.** X-ray diffraction pattern of CdS pure and PPy/CdS composite.

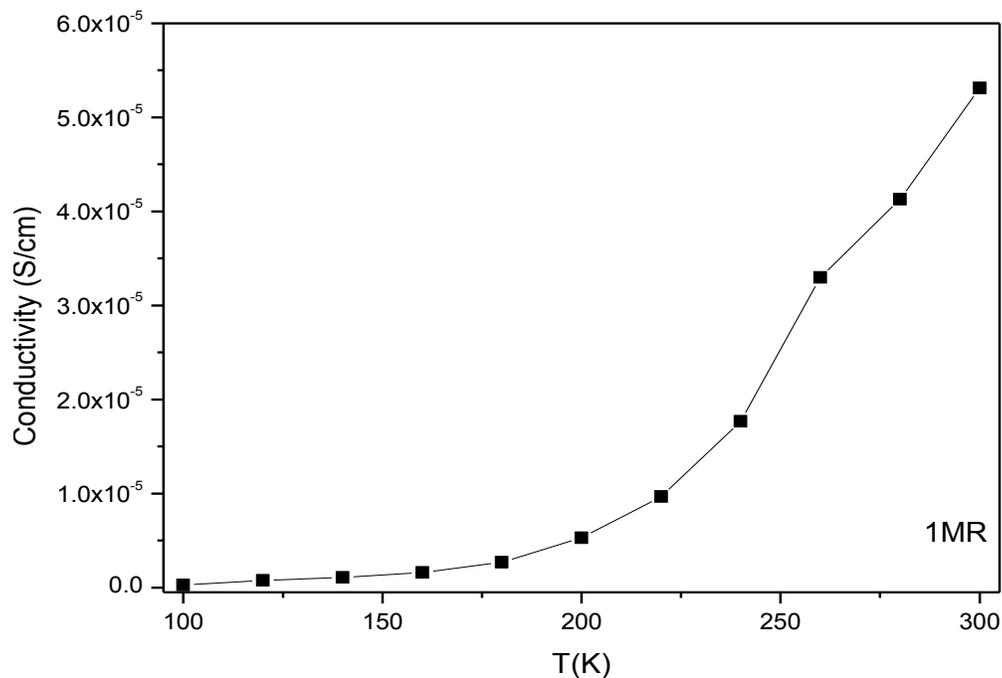
**Table 1.** Comparison of the ICSD  $d$ -spacing data to the experimentally observed values for the PPy/CdS composite with various CdS percentage in 1 MR.

Percentage of CdS (%)	$2\theta$ (°)	$d$ -spacing (Å)		FWHM (°)	h	k	l
		Observed values	Standard values				
CdS pure	24.88	3.58	3.58	0.10	1	0	0
	26.57	3.35	3.35	0.13	0	0	2
	28.26	3.16	3.16	0.13	1	0	1
	36.68	2.45	2.45	0.16	1	0	2
	43.74	2.07	2.07	0.16	1	1	0
	47.89	1.90	1.90	0.13	1	0	3
2	24.74	3.60	3.58	0.23	1	0	0
	26.43	3.37	3.35	0.13	0	0	2
	28.13	3.17	3.16	0.13	1	0	1
	36.54	2.46	2.45	0.26	1	0	2
	43.65	2.07	2.07	0.19	1	1	0
	47.83	1.90	1.90	0.26	1	0	3
4	24.81	3.58	3.58	0.13	1	0	0
	26.47	3.35	3.35	0.13	0	0	2
	28.15	3.16	3.16	0.13	1	0	1
	36.61	2.45	2.45	0.19	1	0	2
	43.66	2.07	2.07	0.26	1	1	0
	47.81	1.90	1.90	0.19	1	0	3
6	24.90	3.58	3.58	0.13	1	0	0
	26.56	3.36	3.35	0.16	0	0	2
	28.25	3.16	3.16	0.13	1	0	1
	36.67	2.45	2.45	0.19	1	0	2
	43.77	2.07	2.07	0.19	1	1	0
	47.90	1.90	1.90	0.10	1	0	3
8	24.87	3.58	3.58	0.13	1	0	0
	26.56	3.36	3.35	0.16	0	0	2
	28.23	3.16	3.16	0.13	1	0	1
	36.67	2.45	2.45	0.13	1	0	2
	43.78	2.07	2.07	0.19	1	1	0
	47.88	1.90	1.90	0.13	1	0	3
10	24.77	3.59	3.58	0.13	1	0	0
	26.45	3.36	3.35	0.13	0	0	2
	28.14	3.16	3.16	0.13	1	0	1
	36.53	2.45	2.45	0.13	1	0	2
	43.62	2.07	2.07	0.16	1	1	0
	47.80	1.90	1.90	0.16	1	0	3

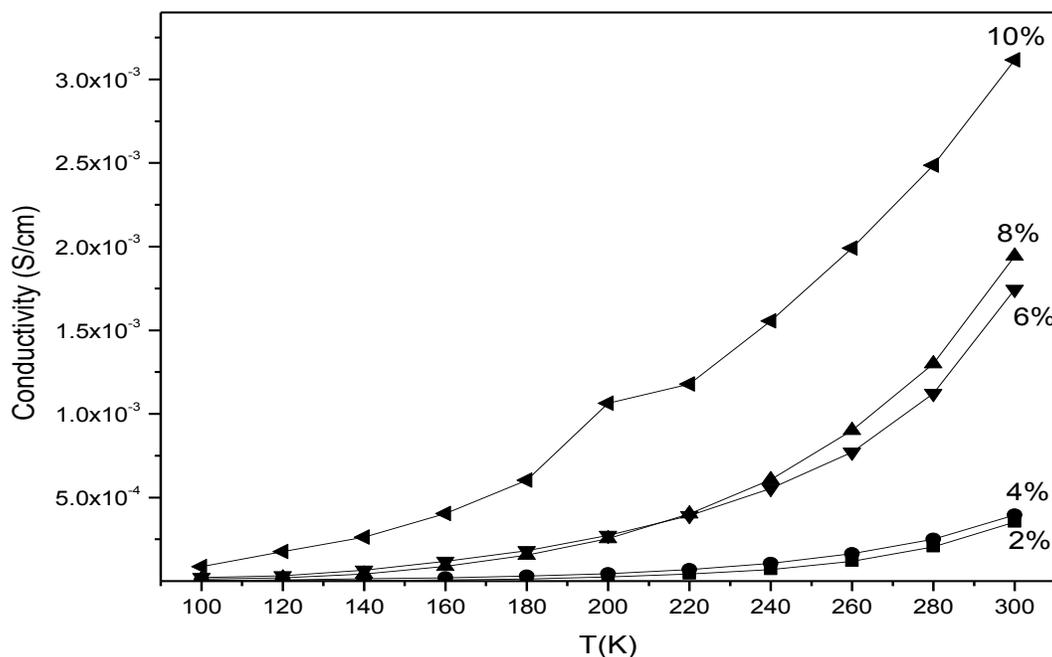
$\times 10^{-5}$  S/cm in the low temperature range of 100 to 300 K.

The electrical conductivity of PPy/CdS composites with 2 to 10% CdS containing 0.2 M pyrrole and 0.2 M dopant concentration measured at low temperature are as shown in Figure 4. We observed that the conductivity value

increases as the CdS percentage increases. It appears that the DC conductivity depend on the temperature on the PPy/CdS composites. The lower value of conductivity as compared to higher value conductivity may be due to the bulky nature of the dopant species, which hinders its



**Figure 3.** Conductivity of conducting polymer PPy with 1 MR at low temperature.

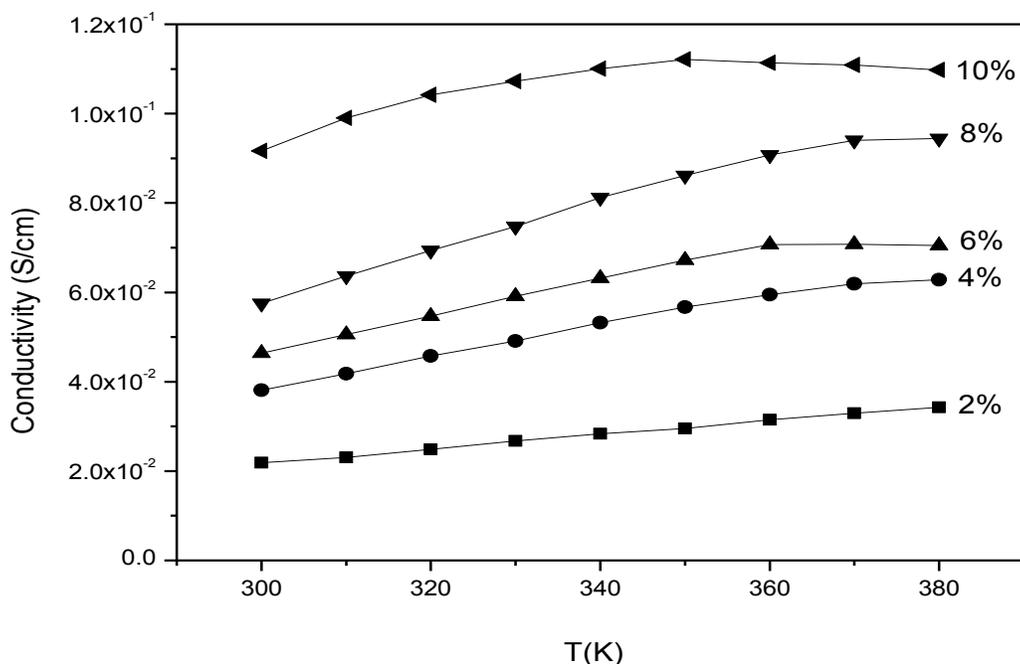


**Figure 4.** Conductivity of PPy-CdS composite with 1 MR at low temperature.

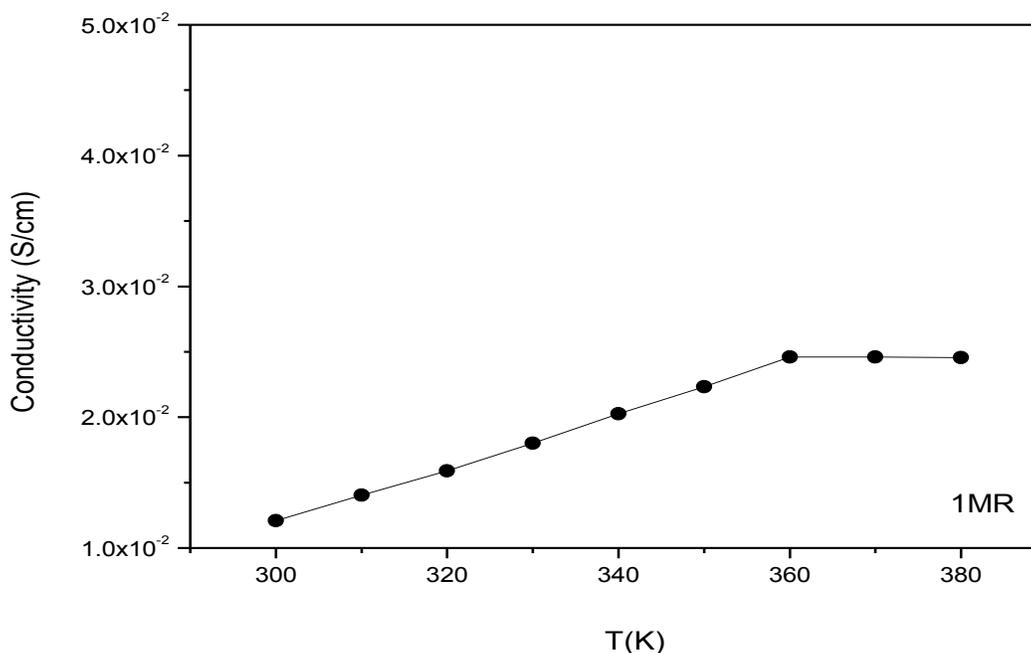
easy diffusion into the polymer backbone (Paul and Raji 2001). There was also the possibility of crosslinking between the chains or interchain sharing of the same dopant species, which resulted as a hindrance to electron

transport. The conductivity that increases from 2 to 10% of CdS at 100K was  $9.26 \times 10^{-7}$  to  $8.74 \times 10^{-5}$  S/cm for 1 MR.

The use of four leads insures that only the potential



**Figure 5.** Conductivity of PPY-CdS composite with 1 MR at high temperature.



**Figure 6.** Conductivity of conducting polymer PPY with 1 MR at high temperature.

drop across the sample is measured (Yi et al., 2000). The variation of the conductivity as a function of the CdS percentage for the PPY/CdS composites measured at high temperature is as shown in Figure 5. Each figure displays the dependence of the conductivity on temperature in the temperature interval of 300 to

380K for 1 MR PPY/CdS composites (Figure 6). From the results obtained in Figure 5, the conductivity was found to increase with increase in CdS concentration from 2 to 10% for the 1 MR. The conductivity value of PPY/CdS composite at 300K increases from  $2.62 \times 10^{-2}$  to  $1.10 \times 10^{-1}$  S/cm as the CdS percentage increases from 2 to

10%. At 10% of CdS, the conductivity increased abruptly as compared to other percentage. The role of CdS on the pellet formation of PPy/CdS composite shows that CdS acts as a co-dopant in the main dopant  $\text{FeCl}_3$  which may take part in the charge compensation of pyrrole repeat units along with  $\text{FeCl}_3$ . Keeping the dopant ( $\text{FeCl}_3$ ) concentration unchanged, the conductivity of the prepared PPy/CdS increases with increasing CdS concentration in the pyrrole. Increasing dopant content had increase in the crystallinity of the PPy/CdS composite and results in increase in conductivity values. This phenomenon had been studied earlier by Yunos et al. (2010) on crystallite size changes of  $\text{Cu}_2\text{SnSe}_3$  thin films when annealed at different annealing temperature.

### Conclusion

The conducting polymer PPy/CdS composites have been successfully synthesized using chemical reaction method. The study on electrical properties of conducting polymer PPy is carried out as a comparison to PPy/CdS composites measured under low and high temperature dependence. The structural and electrical properties of the conducting polymer (PPy/CdS) composites show strong dependence on the reaction method and CdS percentages. It revealed that the electrical conductivity of conducting polymer (PPy) is lower as compared to the PPy/CdS composites.

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