

Electrical Properties of Functionally Upgraded Conducting Polyaniline with Copper Phthalocyanine

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Abstract

Polyaniline (PAni) and Copperphthalocyanine (CuPc) were synthesized by chemical route. These compounds were characterized by FT-IR, UV-Visible spectroscopy. Polyaniline (PAni) was mixed with Copperphthalocyanine (CuPc) with different concentrations on volume to volume basis. Electrical property such as resistivity is checked with different combinations. It is found that combination of PAni and CuPc with different concentration shows change in resistance.

Key Words: PAni, CuPc, composites, resistance

Introduction:

Polymers were seen as good electrical insulators and most of their applications had valid on their insulating properties. Early studies showed that out of the group of polymers some of them exhibit signs of conductivity such as Polypyrroles, Polyaniline, Polythiophene. Since this discovery reported by Shirakawa et al, conducting polymers (CPs) received much attention in the field of science. Out of the other conducting polymers, Polyaniline is widely used one due to its ease of preparation, highly physical and chemical stabilities. It acts as a semiconductor or a conductor. It has π electron delocalization along its polymer backbone; hence it shows unique optical and electrical properties.

There is another class of organic semiconductors such as metallophthalocyanines, which shows interesting and valuable potentialities for conducting applications. Phthalocyanine is a beautifully symmetrical 18- π electron containing aromatic macrocyclic, structurally similar to porphyrin system. Unlike porphyrin, this can be found, in the nature such as hemoglobin in animals, chlorophyll in plants and vitamin - 12. Their physicochemical properties confirm them as most important; small molecular weight organic material ever used. The properties such as high thermal and chemical stability compared with other similar organic materials, a rich substitution chemistry and very practical processability to build devices, leads this material to use as conducting

and sensing of various materials and gases respectively.

Present paper describes a phenomenon of composites of PANi with CuPc. In this, PANi is conducting material and that of CuPc is semiconducting one. The composite of PANi with CuPc shows interesting results. Both PANi and CuPc were synthesized by chemical route. The synthesized powders of PANi and CuPc were characterized by FT-IR and UV techniques. Their resistivity was measured by Keithley Electrometer. The comparative study of PANi, CuPc and composites of PANi with CuPc shows remarkable evidences in order to lead towards further electrical as well as sensing properties in the future.

Experimental Details:

1) Synthesis of Polyaniline (PANi):

Polyaniline is synthesized by chemical route by using aniline (monomer), oxidizing agent (potassium persulphate) and sulphuric acid (H_2SO_4). The reaction is mainly carried out in acidic medium at pH between 0 - 2. The chemical oxidative polymerization of aniline has been carried out in aqueous solution at temperature of $0^\circ C$ in ice bath by dissolving aniline in a strong acidic solution using 1M H_2SO_4 . The polymerization is initiated by drop wise addition of aqueous potassium persulphate solution. The reaction is highly

exothermic. When chemical oxidant was added to aniline in a reaction vessel and left for a certain period of time under stirring, the solution gradually becomes coloured and greenish black precipitate appears. The colouration of the solvent was possible due to the formation of soluble oligomers. The polymer synthesized by chemical method was then isolated from the reaction medium by filtration. The precipitate was then washed and conditioned using an appropriate solvent depending on the nature of the studies that has to be carried out.

2) Synthesis of Copperphthalocyanine (CuPc):

Copperphthalocyanine (CuPc) was synthesized by using Phthalic anhydride, urea and as copper sulphate in 4:4:1 ratio. Phthalic anhydride, urea and metal salt were mixed together and crushed using mortar and pestle into the form of fine powder. The mixture was then slowly heated in the evaporating dish with continuous stirring, the reaction takes place at about $250^\circ C$ to $300^\circ C$ and sufficient heat was generated to maintain the reaction temperature. After completion of the reaction, the residue was washed with distilled water and methyl alcohol many times for purification. The powder form then dried under IR lamps for about half an hour and then crushed with mortar and pestle to make fine grains. In the process of synthesis of

CuPc, the cyclotetramerization reaction takes place at about 250°C to 300°C temperatures. Washing with methyl alcohol and distilled water enables the removing of the precursors to yield the final product in pure form.

3) Pellet Making:

The powder is compacted in the form of pellet using press technique. Pellets were prepared using low cost equipments such as hydraulic press and a die set with optimized parameters. The synthesized PANi and CuPc material were compacted into the pellet form of 13mm diameter under optimized pressure and time using press technique for different concentrations as shown in table 1. These pellets were then used for studying the electrical properties by measuring their resistivity. While making such pellets, three parameters viz. pressure, time and weight of sample material were optimized.

Table 1: Sets of various composites

Set	CuPc (%)	PAni (%)
a	200	0
b	180	20
c	160	40
d	140	60
e	120	80
f	100	100
g	80	120
h	60	140
i	40	160
j	20	180

k	0	200
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4) Resistivity Measurement:

The resistance of each pellet was measured by making an electrode contact on the surface of 10mm diameter pellet with the help of Keithly Electrometer of 2401 series. The resistance of the pellets gets varied in decreasing manner as the concentration of the PANi in CuPc has been changed, shown by the electrometer.

5) Characterization:

5a. FTIR Spectra:

The synthesized Polyaniline is characterized by FT-IR spectroscopy. FT-IR spectra were recorded using Thermo Nicolet iS5, iD1 transmission FT-IR spectrometer by KBr pellet method as well as ATR facility in the region 500-4000 cm⁻¹.

5b. UV Visible spectra:

The UV- visible spectrum of chemically synthesized PANi, CuPc and composites of PANi with CuPc were recorded by using UV-visible spectrometer, Evolution 201, Thermo scientific. In case of CuPc, it originates from molecular orbital within the aromatic 18 π electron system and from overlapping orbital within the central atom. All spectra display the existence of strong absorption bands in the range 350 nm to 650 nm caused by the π - π^* transitions of the conjugated macrocycle of

18π -electrons. The high energy side of the absorption spectrum shows a sharp absorption edge. The central metal atom of the phthalocyanine influences the optical absorption spectrum.

6) Result and Discussions:

a) FT-IR of PAni:

Figure 1.1 below shows FT-IR spectrum of chemically synthesized PAni. The peak observed at 3440.18 cm^{-1} is attributed to N-H

stretching vibrations. The characteristic bands at 2928.27 cm^{-1} is corresponding to C-H stretching. The peak observed at 1559.83 is mainly due to C=N & C=C stretching vibrations of the quinoiddiamine unit. The band around $1475\text{-}1479\text{ cm}^{-1}$ is attributed to the C=C ring stretching of the benzoiddiamine unit. The bands around 1298 & 798 cm^{-1} can be assigned to C-N stretching of the secondary aromatic amine and aromatic C-H out of plane bending modes respectively.

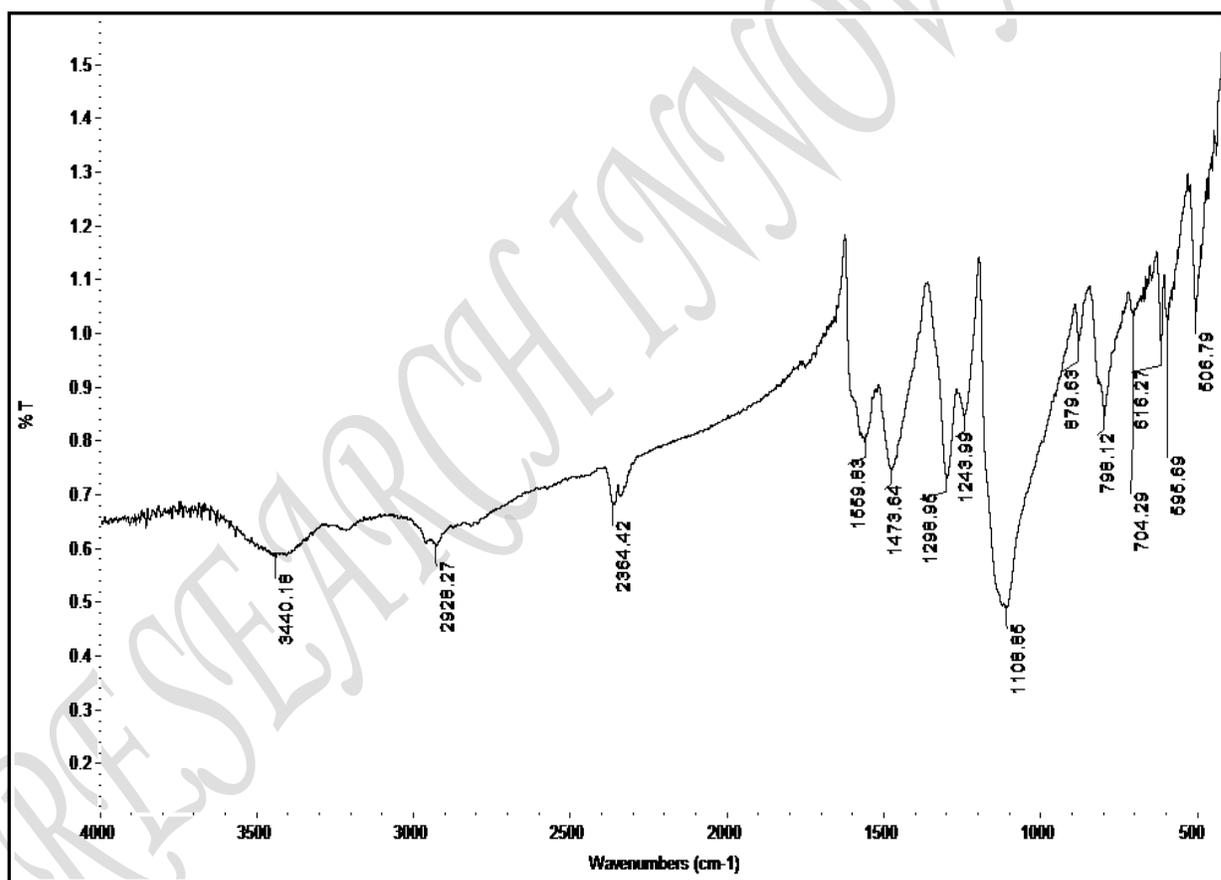


Figure1.1: FTIR spectra of PAni

b) FT-IR of CuPc:

Figure1.2 shows FT-IR spectra of chemically synthesized CuPc. The region between 500 cm^{-1}

to 1800 cm^{-1} corresponds to the skeleton of metallophthalocyanine. The change in spectral range from 1800 cm^{-1} to 3500 cm^{-1} was due to

the Cu metal incorporated centrally in the phthalocyanine. A series of weak absorption was observed between 3000 cm^{-1} to 3500 cm^{-1} . The bands appearing at 1183 cm^{-1} , 1252 cm^{-1} , 1287 cm^{-1} , and 1307 cm^{-1} are assigned due to the C-N in isoindole and in plane band stretching vibration. The band corresponding to C-C stretching (isoindole) was observed at 1387 cm^{-1} . The bands appearing at 817 cm^{-1} and

745 cm^{-1} were assigned to the C-H bending out of plane deformations. The peaks observed in the range 700 cm^{-1} to 500 cm^{-1} interval originates from the vibrations in the benzene ring interaction with the pyrrole ring. The peak at 793 cm^{-1} was due to C-N stretching vibration and that of peak at 715 cm^{-1} indicates the macrocycle ring deformation.

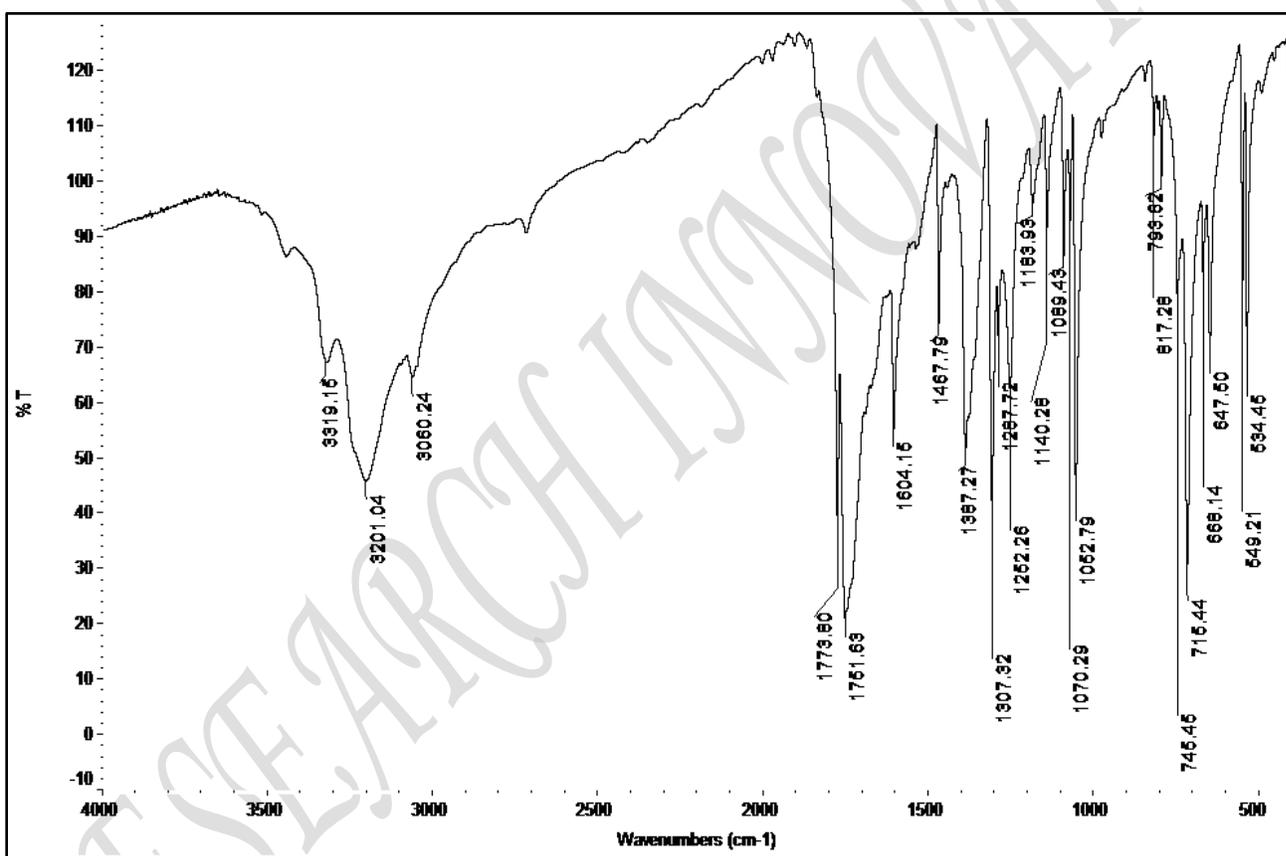


Figure 1.2: FT IR spectra of CuPc

c) FT-IR of Composite of PANi + CuPc:

The figure 1.3 below shows the FT-IR of composite of PANi with CuPc. It was observed that many peaks of both PANi and CuPc material were disappeared. Some of them get modified and remaining gets shifted corresponding to their absorbed wavenumbers.

The peak observed at 3029.31 cm^{-1} was due to the C-H stretching. 1651.53 cm^{-1} was due to C=O stretching of primary amides, amide I band. The strong absorption due to O-H in plane deformation was assigned at 1403.22 cm^{-1} . The wave number 1035.73 cm^{-1} was due to strong absorption sulfonic acid, S=O stretching.

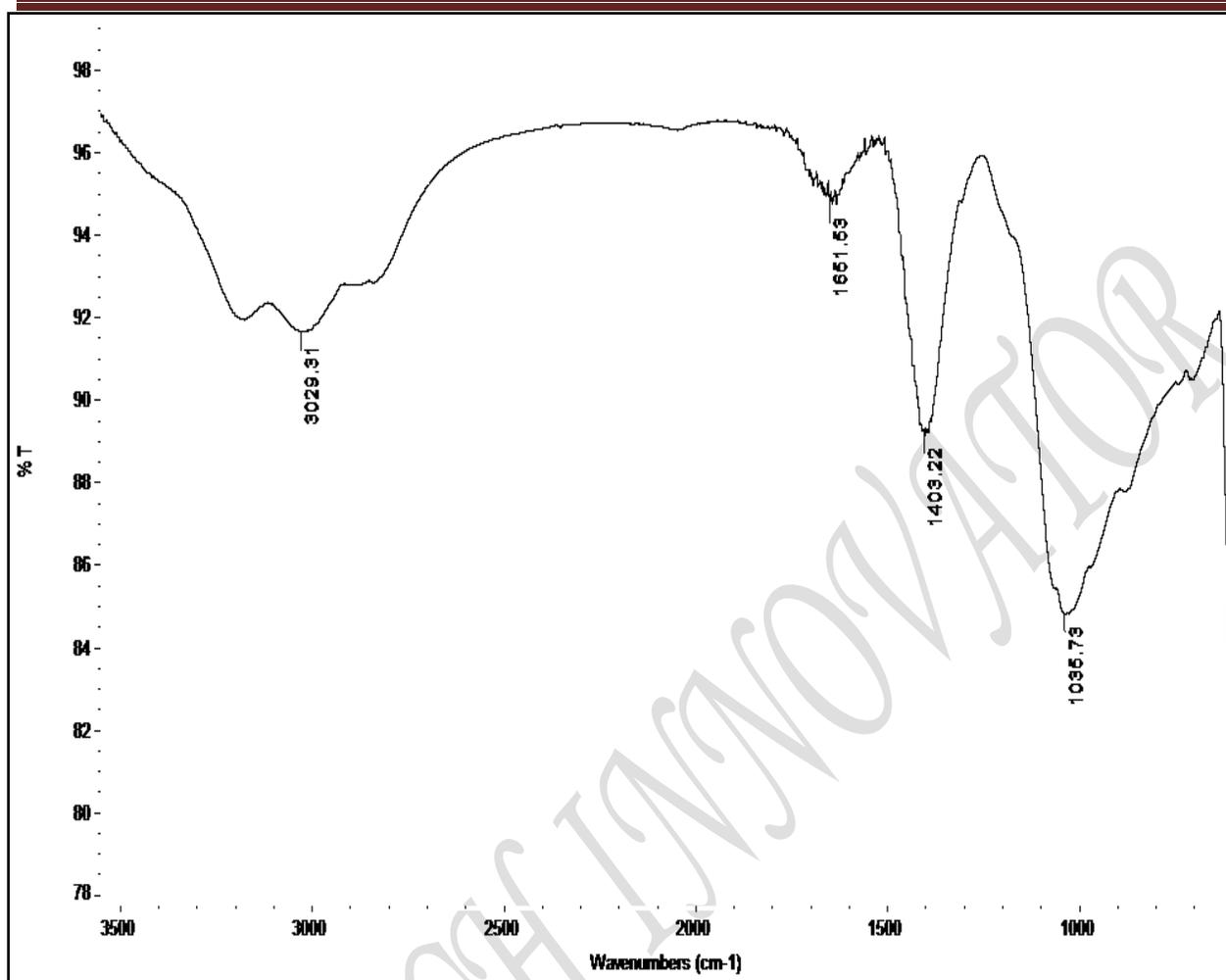


Figure 1.3: FTIR spectra of composite of PANi with CuPc

d) UV-Visible Spectra:

The peak around 584 nm is because of $n-\pi^*$ transition which is in concordant with the diffused reflectance spectra of the polymer surface (or due to excitation formation of quinoid ring corresponding to semi-conducting phase for polyaniline SO_4). The solution of PANi and CuPc was prepared in N-N dimethyl formamide. The broad absorption band in the UV region is preceded by the UV absorption band edge of the phthalocyanine molecule. The absorption bands in the region of 200 nm to 350

nm called as soret a band which indicates the presence of d band associated with the central metal atom. The figure 1.4 (a) shows absorption spectrum of PANi, that of 1.4 (b) was of CuPc and 1.4 (c) shows absorption peak of composite of PANi with CuPc. The corresponding λ_{max} were 584nm, 586nm, 620nm respectively. The bandwidth along with PANi, for $\lambda=478$ nm was $E_g = 2.59$ eV; that of CuPc, for $\lambda=472$ was $E_g = 2.62$ eV and for composite at $\lambda=475$ nm was $E_g = 2.60$ eV; which was average of individual of PANi and CuPc.

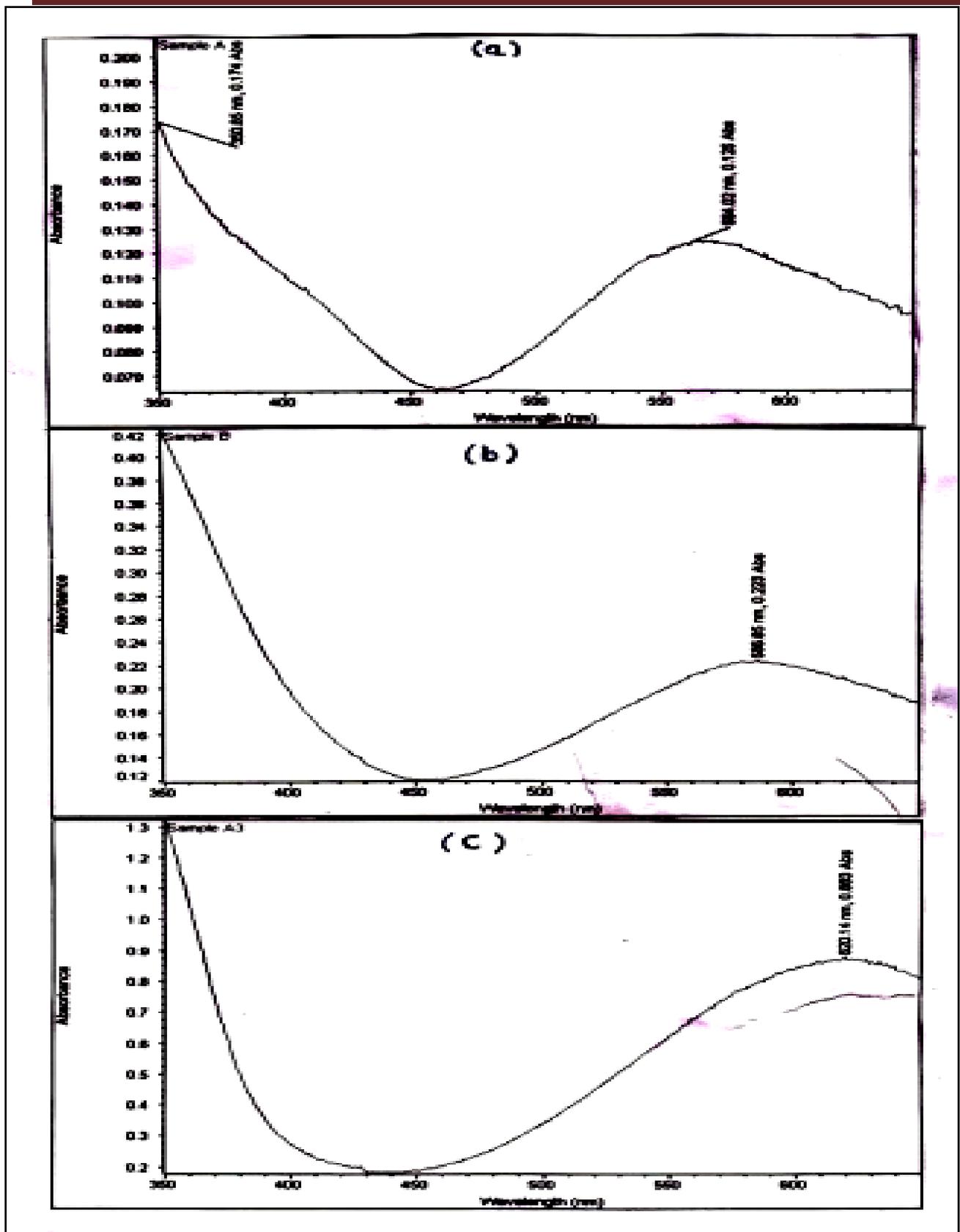


Figure 1.4: UV visible spectra of of(a) PANi, (b) CuPc and(c) PANi and CuPc composite.

e) Resistivity response:

The figure 1.5 shows variation in resistance with respect to increment in PANi concentration with CuPc. It was seen that the resistance of PANi pellet was near about 340-350 k Ω before it

adds with CuPc. When PANi get composite with CuPc in set a, b, c, d, e, f, g, h, I, j, k ; the value of resistance get decreased up to 30-35 k Ω . Hence, it is seen that the number of charge carriers were increased with PANi concentration.

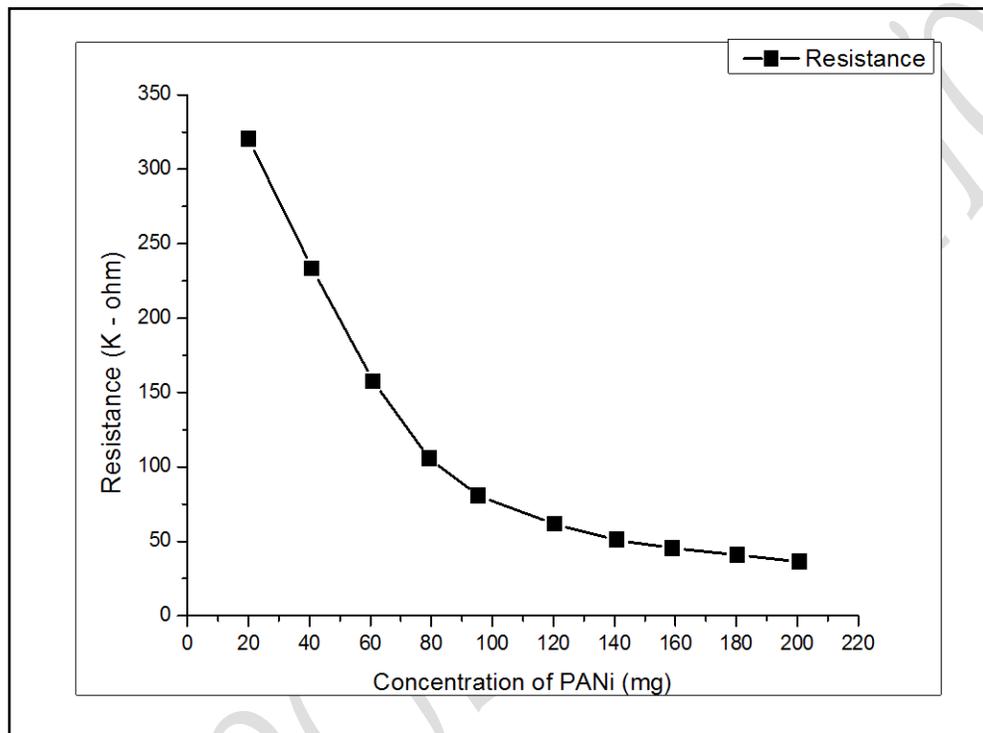


Figure 1.5: Variation of resistance with change in concentration of PANi

7) Conclusion:

The electrical properties of composites of PANi with CuPc have been studied by analyzing FT-IR, UV and Resistivity response. The composite FT-IR spectrum has recorded some modified as well as shifted peaks. The composite UV spectra assign to average bandwidth than that of individual PANi and CuPc. There is increment in charge carriers as the PANi composites with CuPc as above mentioned manner. All this may happen due to

variation in grain sizes or resistances of conducting, semiconducting, insulating combinations in parallel fashion.

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