

Magnetic Properties of CuCl₂ Doped Polyaniline and Determination of Anisotropic Constant

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ABSTRACT

Polyaniline prepared in the chemical synthesis method. It is doped with copper chloride. They were characterized by XRD, FTIR spectroscopy measurements. Room temperature dc magnetic susceptibility is measured. At high magnetic fields the localization of the charge carriers occur but at low magnetic field the delocalization occurs. Anisotropic constant values are calculated.

Keywords: Magnetic susceptibility; electrical conductivity; anisotropy constant

1. Introduction

Conducting polymer with polyaromatic backbone including polypyrrole, polythiophene, polyaniline etc has received a great deal of attention in the last two decades. Among these polymer, polyaniline(pani) has been of particular interest because of its cheap monomer, simple synthesis technology, unique electrochemical properties, high conductivity and environmental stability^{1,5}. In order to obtain materials with superior electrical and magnetic properties we have synthesized polyaniline (Pani) doped with CuCl₂. They are characterized by their xrd and Fourier transform infra-red spectrum, Uv-vis optical absorbance spectrum in Dimethyl sulphoxide as a solvent (DMSO). Magnetic susceptibility was measured.

In multidomain system domain wall movement or rotation determines the magnetization process. And this movement depends on anisotropy which is sensitive function of structure like defects and anisotropy atom etc. so the magnetization and field dependence of susceptibility structure sensitive properties which can be studied by their dependence on external field. In this work the mean of as a function of H has been measured first for a samples like Cu-doped Polyaniline.

The magnetic field required to produce the, saturation varies according to the relative geometry of the field to easy axis and other metallurgical conditions of the materials. In the other words, the approach to saturation is a structure sensitive process. The field depends on magnetization fitted empirically by the relation⁶

$$M(T, H) = M_s(T) \left[1 - \frac{a(T)}{H} - \frac{b(T)}{H^2} \right] + C(T)H^n \quad \dots(1)$$

where $n = 1$ for crystals
 $= 1/2$ for amorphous and

$M_s(T)$ is spontaneous magnetization at a temperature T . $a(T)$, $b(T)$ and $c(T)$ are constant at a given temperature T . The last term of the above equation is due to the paraprocess⁷. According to (1) the contribution of the paraprocess becomes small at low fields and the term of microstructure are dominant. On other hand at large fields the paraprocess dominates and the terms resulting from the macrostructure vanishes.

Therefore when the field is small, magnetization can be written

$$M(T, H) = M_s(T) \left[1 - \frac{a(T)}{H} - \frac{b(T)}{H^2} \right] \tag{2}$$

The term a/H and b/H^2 were attributed to the stress field around dislocation and voids due to no magnetic inclusion, respectively. For polycrystalline material the parameter is related to anisotropy constant.

$$b = \frac{8}{105} \left(\frac{K^2}{M_s \mu} \right) \tag{3}$$

where $\mu_0 =$ permeability in free space.

From equation (2) and differentiating this equation with respect to H_1 we get

$$\sum \frac{X_i(T, H)}{H_i^2} = \sum \frac{M_s(T) \left[\frac{a(T)}{H_i^3} + \frac{b(T)}{H_i^4} \right]}{H_i^3} \tag{4}$$

From equation (2) and (4) we get the matrix equation of

$$\begin{pmatrix} \sum \frac{1}{H_i^4} & \sum \frac{1}{H_i^5} \\ \sum \frac{1}{H_i^5} & \sum \frac{1}{H_i^6} \end{pmatrix} \begin{pmatrix} \frac{a(T)}{M_s} \\ \frac{b(T)}{M_s} \end{pmatrix} = \begin{pmatrix} \sum \frac{X_i}{H_i^2} \\ \sum \frac{X_i(T, H)}{H_i^3} \end{pmatrix}$$

Solving above equation we get the temperature dependent coefficients $a(T)$, $b(T)$ and $M_s(T)$ using equation and then anisotropy constant(K) can be calculated from equation(3).

2. Experimental

Aniline (Merck) was double distilled under vacuum and 0.1(N) solution of different dopants were prepared. 2 ml aniline mixed with 48 ml double distilled water. 50 ml 0.1 (N) of dopant solutions mixed with aniline water mixture with continuous magnetic stirring. Required amount of precooled (0°C) aqueous solution of ammonium peroxodisulphate added to the mixture with continuous stirring for 2 hours and left at rest to polymerize for 24 hours. The polymer obtained was centrifuged and washed with water and acetone to remove the unused oxidant and the oligomer produced. The samples were dried in an oven overnight at 30°C.

The structural characterization of pure and doped polyaniline were carried out in PW3040180X Pert pro analyzer using Cu K_α radiation ($\lambda=1.5406\text{\AA}$). The x-ray diffraction studies were conducted on all the samples in the 2θ ranges from 20° to 80° . The infrared spectra of the doped and undoped polyaniline samples were taken in KBr pellets using a Matsonn 1000 FTIR spectrophotometer. The Uv-vis absorption spectra of the samples were taken by a double beam spectrophotometer (Systronics) 2101 model using Dimethyl sulphoxide as a solvent.

A glass test tube filled up to a certain height (18 cm) with the sample is suspended from an arm of a sensitive balance (Gouys method) such that the bottom part of the sample is in a strong magnetic field and the top part is no vibrational and air disturbance. Usually an electromagnet giving a constant magnetic field (H) in the range of 1000 to 5000 gauss is used. The Force experienced by the sample is measured by the change in weight. Thus the susceptibility per gm is calculated by the equation (1)

$$X_g = 2l (\delta m) g / mH^2$$

where m and l represent the mass and the length of the sample, δm =change in mass due to the imposition of the magnetic field. X_g (magnetic susceptibility) for two rings of doped polyaniline were determined after diamagnetic correction of glass. The samples marked as A and B are undoped polyaniline, Copper Chloride doped polyaniline respectively.

3. Results and Discussions

Fig-1: XRD pattern of the polyaniline/CuCl₂ composite is shown in fig-1. A broad peak at $2\theta=23^\circ$ is observed showing polyaniline is amorphous. Meanwhile, the XRD of the polyaniline/CuCl₂ composite also exhibit sharp peaks showing cubic structure of CuCl₂⁸.

Fig-2 shows the Fourier transform i.r.spectra of undoped polyaniline and doped polyaniline polyaniline. The spectrum exhibited several characteristic peaks at 3450,1600,1500,1291,1109,795 cm⁻¹. These peaks were attributed to the N-H stretching of secondary amine, benzoid ring stretching, C-N stretching band, vibrations of the dopant anion, and paradisubstituted benzene, respectively. The decrease in peak area with respect to polyaniline indicates the structural change in the polymer due to doping⁹⁻¹².

Fig-3 shows the UV-vis absorption spectra of different samples in solution. The spectrum of the polymers mainly consists of three absorption bands at 280-330nm, 390-405nm and 575-620nm respectively. The first band is due to $\pi-\pi^*$ transition in the benzoid rings and the other two bands are due to exciton absorption of the quinoid rings respectively¹³. In case of doped polyaniline a blue shift occurs from 330nm to 290nm occurs due to the doping of CuCl₂ in polymer backbone.

Fig-4 shows that with increase of the magnetic field the magnetic susceptibility decreases for both the undoped and doped polyaniline. It is interesting that the magnetic susceptibility decreases more for the undoped polyaniline than the doped polyaniline with increase in the magnetic field. In case of Cu-doped polyaniline, the magnetic susceptibility first decreases with increase in magnetic field and then susceptibility remains almost same with positive susceptibility and in case of undoped polyaniline the magnetic susceptibility first decreases and then it become negative with increase in magnetic field .At high magnetic field the localization of

the charge carrier occur but at low magnetic field the delocalization of the charge carrier occur.

The anisotropy constant values are given in Table-1 for different samples.

Table 1. Anisotropy constant (K) of doped polyaniline in cgs unit.

Field	K of Cu doped Polyaniline
1Kgauss	2.3×10^4

4. Conclusion

The magnetic susceptibility of the polyaniline and doped polyaniline are measured and from the magnetic susceptibility values anisotropy constants of doped polyaniline is calculated. Suitable magnetic ion doping could change the anisotropic constant values and this change of anisotropic constant values can also change magnetization process. Thus controlling the anisotropic constant values we can prepare different tailored made magnetic materials for technology.

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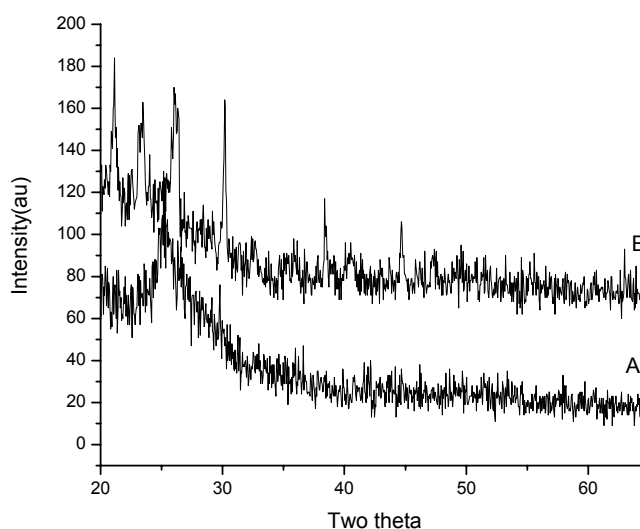


Fig 1: XRD of polyaniline and CuCl_2 doped polyaniline

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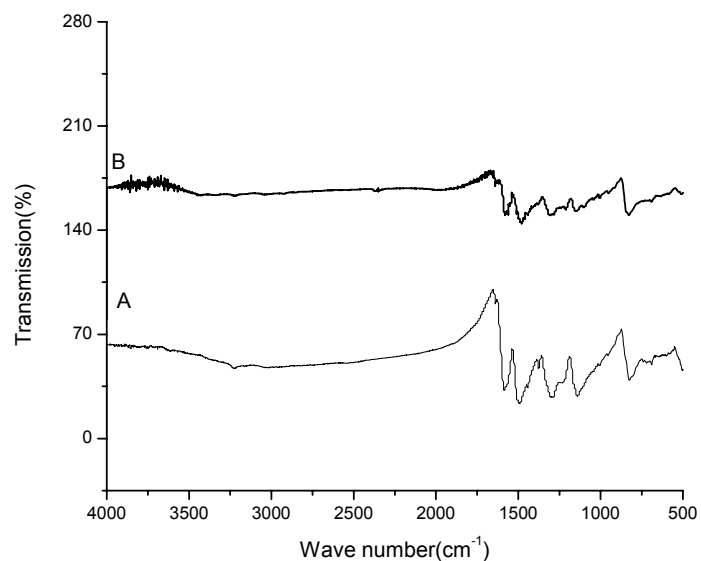


Fig2: Fourier transform infra red spectrum of polyaniline and doped polyaniline

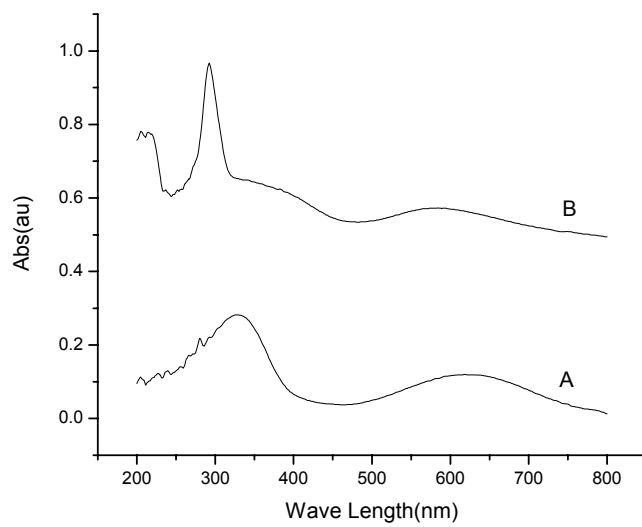


Fig3: Uv-vis spectrum of polyaniline and CuCl_2 doped polyaniline

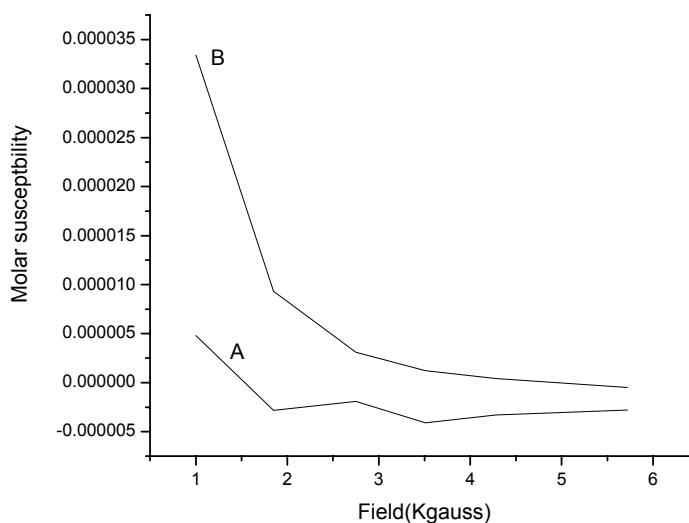


Fig4: Magnetic susceptibility of polyaniline and CuCl_2 doped polyaniline

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