

Thermal Properties of CuO doped Polyaniline

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Abstract-This paper provides thermal properties of chemically synthesised Polyaniline and its CuO doped composites with various doping levels. Structural property was observed by XRD which confirms the synthesis of the polyaniline and CuO doped polyaniline composite. The main peaks in the XRD pattern of pure PANI are observed at $2\theta = 15.53^\circ$ and the other characteristic peaks ascertained from the XRD pattern of PANI/CuO nanocomposites are at $2\theta = 35.54^\circ, 38.71^\circ, 48.94^\circ$. The diffraction peaks at 2θ values of $35.54^\circ, 38.71^\circ$ and 48.94° corresponding to (-1 1 1), (1 1 1) and (-2 0 2) which shows the stability of the polymers. Thermal properties were measured out using DSC thermograms indicated that there was a glass transition temperature (T_g) at about 85°C and the doping process shifted it towards higher temperature which shows increased thermal stability. DSC plot also indicates occurrence of physical changes like loss of moisture and other ingredients and chemical changes like decomposition depending on the temperature. Two distinct endotherm peaks are observed at around $57^\circ\text{C} - 173^\circ\text{C}$ and $196^\circ\text{C} - 343^\circ\text{C}$ for pure PANI whereas for composites it shifted towards Miller planes.

Keywords DSC, Glass Transition, Polyaniline, XRD.

1. INTRODUCTION

Conducting polymers have a wide range of application areas such as rechargeable batteries, organic field effect transistors, sensors, plastic solar cells and anticorrosive materials due to their unique physical and chemical properties⁽¹⁻¹²⁾. Generally, polymers are known as a class of heat sensitive, flexible, electrically insulating and amorphous or semi crystalline materials. The electrical properties of polymers can be modified by the addition of inorganic materials. Nanoscale particles as fillers are attractive due to their intriguing properties arising from the nanosized and resulting large surface area. The doping of nanoscale materials may improve the electrical and dielectric properties of the host polymers⁽¹³⁾. Among the various conducting polymers, polyaniline (PANI) has received great attention due to its simple preparation, environmental stability, interesting redox behaviour and tunable electro-optical properties⁽¹⁴⁻¹⁷⁾. The electrical properties of conducting polymer could be modified by the addition of inorganic fillers⁽¹⁸⁻²¹⁾. In the present work, chemically synthesized PANI as emeraldine powder form and its composites are characterized by XRD and DSC thermograms and are investigated in details.

2. EXPERIMENTAL

Aniline hydrochloride (2.59 g) was dissolved in distilled water in a volumetric flask to make 50 mL solution. Ammonium peroxydisulfate (5.71 g) was dissolved in water also to make 50 mL of solution. Both the solutions were kept for 1 hour at room temperature. They were then mixed with a brief stirring and left at rest to polymerize. The solution turned to dark green within few minutes. Next day PANI Precipitate was collected on a filter paper, washed three times with 100 mL portions of 0.2 M HCl to remove the uncreated aniline and its oligomers from the precipitate. After this process, precipitate was washed in three times with 100 mL portions of acetone to absorb the water molecules and for the removal of any residual organic impurities. PANI, synthesized by this method, is formed in its protonated state. The precipitate was firstly dried in air for 30 min and then in oven for 3 hours at 60°C . The synthesized PANI was grinded in form of fine powder. Pellets were prepared by compressing the powder under a pressure of 10 tons with the help of a hydraulic press machine.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

XRD spectra recorded for the sample a, b, and c and curves a, b, and c correspond to 0, 10, and 20 wt% CuO doped PANI composites, respectively. Polyaniline is inherently amorphous and hence there are no sharp peaks for Polyaniline. The X-Ray diffraction pattern, Fig. 1(a) indicates that strongly disordered, the PANI shows only a small scattering around $2\theta = 15.53^\circ$ ^(22, 23). The crystalline natures of nano-composites are determined from XRD analysis. The XRD patterns of pure polyaniline and PANI/CuO nano-composites are shown in Fig.1 a, b and c respectively. The main peaks in the XRD pattern of pure PANI are observed at $2\theta = 15.53^\circ$ and the other characteristic peaks ascertained from the XRD pattern of PANI/CuO nano-composites are at $2\theta = 35.54^\circ, 38.71^\circ, 48.94^\circ$. The diffraction peaks at 2θ values of $35.54^\circ, 38.71^\circ$ and 48.94° corresponding to (-1 1 1), (1 1 1) and (-2 0 2) Miller planes are selected for calculating the crystallite size for CuO phase. Similar result of CuO are earlier reported by Abd El-Aziz A.Said et al.⁽²⁴⁾ Crystallite size can be estimated from the full width at half maximum (FWHM) of the X-ray diffraction data. The broadening of the FWHM is inversely proportional to the average

crystallite size, D , as predicted by the well-known Scherer's formula⁽²⁵⁾ The crystallite sized is calculated from the following relation:

$$D = k\lambda/\beta \cos\theta \quad 3.1$$

where, λ , is the X-ray wavelength; k , the shape factor; D , the average diameter of the crystals in angstroms; θ , the Bragg angle in degree; and β is the line broadening measured by half-height in radian. The value of k depends on several factors including the miller index of the reflection plane and the shape of crystal. If the shape is unknown, k is often considered to be 0.89. The crystallite size of PANI/CuO nano-composites are formed to lies between 15-45 nm.

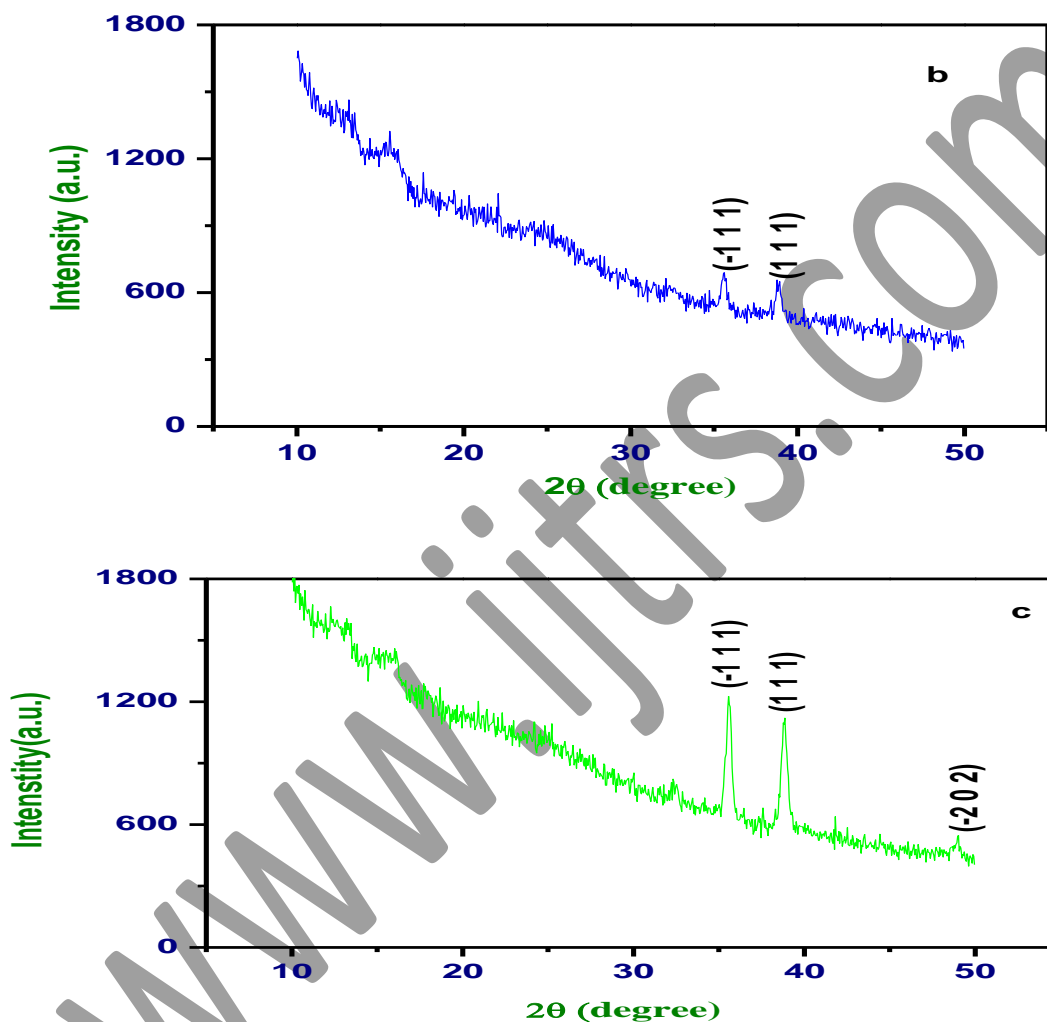


Fig.3.1 XRD Spectra for the Sample a, b, and c and Curves a, b, and c Correspond to 0, 10, and 20 wt% CuO Doped PANI Composites, Respectively

3.2 Thermal Properties

The DSC thermogram in the figure 2 shows two endothermic and one exothermic peak. First peak is obtained at around 89.65°C (glass transition)⁽²⁶⁻³⁰⁾ which is an important characteristic of semiconductor and amorphous materials. Generally, glass transition depends upon the processing of the material as well as materials characteristics such as structure, bonding and molecular weight. Second recrystallization peak of undoped PANI is observed at around 154.706°C which is due to the cross linking of polymers. At this point arrangement of intermolecular bonds form and polymeric molecules becomes more ordered formation of bonds during crystallization is an exothermic process. Therefore peak is observed in thermogram. Third peak is observed at 267.08°C which denotes the degradation point or melting point^(28, 29) of the material. When a material starts to melts its intermolecular bonds absorbs energy and begin to loosen therefore it requires energy. It is an endothermic process. In the presence of CuO,

the peaks are observed to be shifted towards higher temperature which is due to the formation of strong intermolecular bonds and therefore it absorbs more energy to break the bonds.

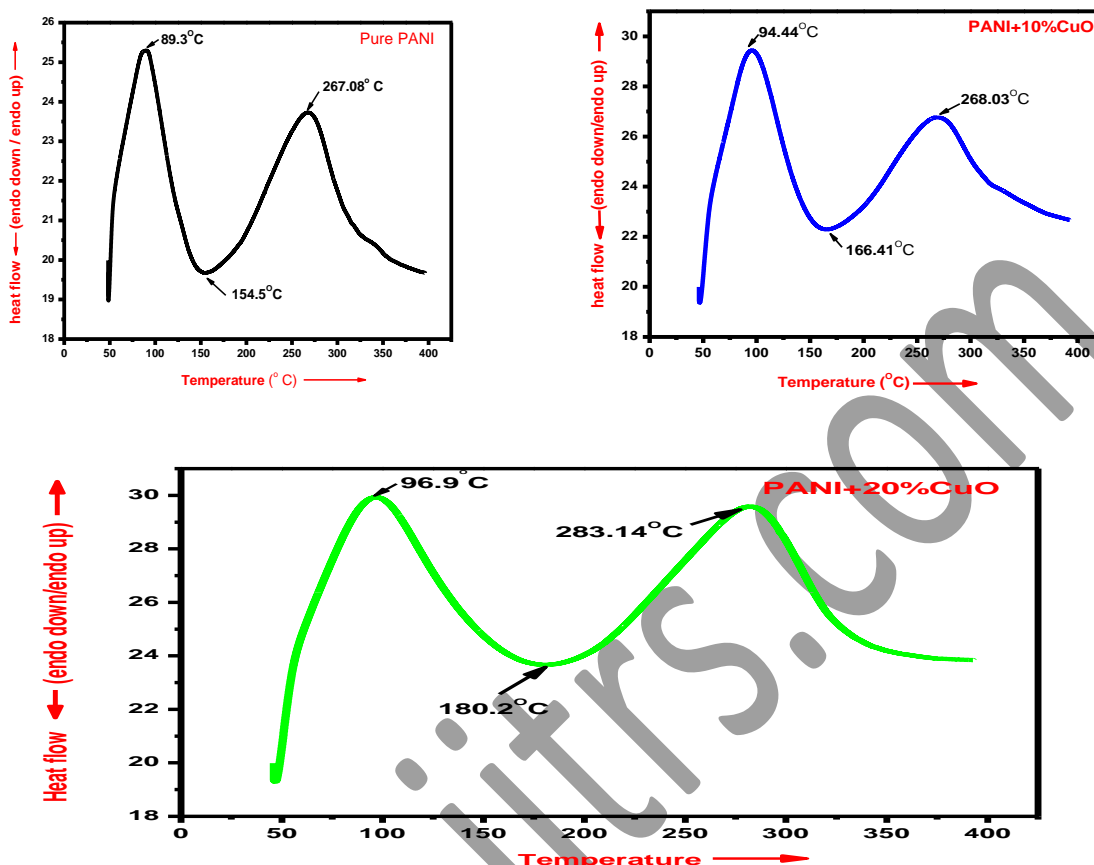


Fig. 3.2 DSC Thermograms for the Sample A, B, And C and Curves A, B, and C Correspond to 0, 10, And 20 Wt% CuO Doped PANI Composites, Respectively

CONCLUSION

Through this study results shows that due to the presence of CuO particles with polyaniline nanocomposite becomes more stable towards higher temperature, understanding of dopant concentrations and their performances in the host material can be helpful for making efficient and reliable models and detectors.

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