

# Humidity Sensing and Electrical Properties of Polyaniline/Cobalt Oxide Composites

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**ABSTRACT:** Polyaniline/cobalt oxide composites were synthesized by an *in situ* chemical polymerization method with ammonium persulfate as an oxidizing agent. This was a single-step polymerization process for the direct synthesis of the emeraldine salt phase of the polymer. The polymers were characterized with X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectral analysis. The formation of mixed phases of the polymer together with the conducting emeraldine salt

phase was confirmed by spectroscopic techniques. High-temperature conductivity measurements showed thermally activated behavior. A change in the resistance was observed with respect to the relative humidity when the pellets were exposed to a wide humidity range of 10–95%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 653–658, 2007

**Key words:** conducting polymers; sensors; synthesis

## INTRODUCTION

Conductive polymeric materials containing conjugated  $\pi$  bonds have attracted much interest in scientific and technological areas in recent years. Conducting polymers such as polypyrrole, polythiophene, poly(*p*-phenylene), and polyaniline (PANI) have commonly been used in scientific and industrial studies and in various applications such as rechargeable batteries,<sup>1,2</sup> sensors,<sup>3–6</sup> diodes, transistors, and microelectronic devices.<sup>7</sup> Among these polymers, PANI is unique because of its high electrical conductivity, good environmental stability, and easy preparation.<sup>8,9</sup> As a result, it has been studied extensively and has emerged as the most promising candidate for commercial applications. However, a major problem related to its successful utilization lies in its poor mechanical properties and processibility due to its insoluble nature in common organic solvents. The preparation method of PANI involves two main techniques (chemical and electrochemical polymerization) using suitable protonation media. A number of publications are available reporting the synthesis of PANI with different dopants and its characterization.<sup>10,11</sup>

Also, polymer/single-wall carbon nanotube composites have attracted tremendous attention<sup>12,13</sup> because of their unique electronic and mechanical properties for potential use in future spacecraft. Next-generation spacecraft will require ultra-light-weight materials that possess specific and unique combinations of properties, such as radiation and atomic oxygen resistance, low solar absorptivity, high thermal emissivity, electrical conductivity, tear resistance, and the ability to be folded and seamed.

In recent years, inorganic semiconducting oxides such as zinc oxide (ZnO), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), titanium oxide (TiO<sub>2</sub>), tin oxide (SnO<sub>2</sub>), and iron oxide (Fe<sub>2</sub>O<sub>3</sub>) have been studied extensively and have emerged as economical sensors for monitoring toxic gases and humidity.<sup>14–17</sup> The sensitivity of these sensors to gas and humidity depends on their microstructure. This can be achieved with special techniques of preparation or via doping with impurities. The doping of SO<sub>4</sub><sup>2-</sup>, Ti, Sn, Zn, Si, and so forth in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can improve the sensing capabilities.<sup>18–21</sup> In general, metal oxides have good chemical and thermal stability. Sensors based on changes in the resistance and capacitance are preferred to conventional ones because of their compact size, which could facilitate the miniaturization required for electronic circuitry. Of these, a disc-type sensor offers higher sensitivity toward humidity than a thin film because of its larger capacity for water absorption.

The electrical response with humidity variations has been attributed to both chemisorption and capil-

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lary condensation of water molecules. Over the years, a great many sensing methods have been developed for measuring a variety of humidity-related parameters. Each of these has unique advantages and limitations and is suitable only in certain applications. A relative humidity (RH) range of 0–100% corresponds to a water vapor pressure span of about  $0.8 \times 10^{-6}$  to 760 mmHg for saturated steam, that is, a dynamic range of  $10^9$ . No single sensor is capable of covering this entire range.<sup>22</sup> The range of applications in which humidity measurements are needed is endless and is increasing with time as new information is required on the effects of humidity on quality, cost, safety, comfort, and human health. The conventional materials used for sensing humidity are electrolytic metal oxides, alumina thin films, and ceramics.<sup>23</sup> However, polymers are identified as good candidates for practical applications because they are compatible with oxides and ceramics, because of their low cost, flexibility, light weight, and easy processibility, and because they can be used at room temperature.<sup>24,25</sup> Various polymers have been used to prepare humidity sensors. From their basic principles, they are classified into two categories based on (1) changes in the electrical properties of the materials due to the absorption of water vapor and (2) gravimetric changes in the materials, such as quartz crystal oscillators. The first category is divided into two types: electric-resistance type and capacitor type. Hydrophilic polymers are used for resistance-type humidity sensors, whereas hydrophobic polymers are preferred for the capacitance type. Nowadays, a variety of polymers doped with suitable molecules or dyes are being used in optical humidity sensing.<sup>26</sup>

In our earlier studies on electrical and humidity sensing with PANI/WO<sub>3</sub>, we reported good humidity sensitivity for a broad humidity range (10–95% RH).<sup>27</sup> In this work, we report a study on the preparation, characterization, and successful utilization of PANI/cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) composites as humidity sensors.

## EXPERIMENTAL

The monomer aniline was doubly distilled before use. Ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], hydrochloric acid (HCl), and Co<sub>3</sub>O<sub>4</sub> (Sigma) were analytical-reagent-grade and were used as received.

Aniline (0.1 mol) was dissolved in 1M HCl to form an aniline solution. Co<sub>3</sub>O<sub>4</sub> was added to the aniline solution with vigorous stirring to keep Co<sub>3</sub>O<sub>4</sub> suspended in the solution. To this reaction mixture, 0.1M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, which acted as the oxidant, was added slowly with continuous stirring at 0–5°C. After the complete addition of the oxidizing agent, the reaction mixture was kept under stirring for 24 h. The greenish-black precipitate of the polymer was recovered by vacuum filtration and washed with deionized water.

The resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

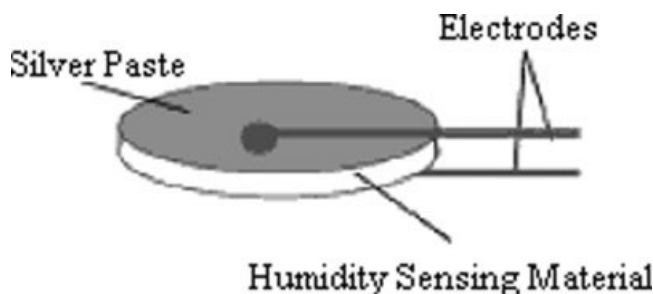
PANI/Co<sub>3</sub>O<sub>4</sub> composites were prepared in a weight percentage ratio in which the concentration of Co<sub>3</sub>O<sub>4</sub> (10, 20, 30, 40, and 50 wt %) was varied. The test samples to be used as sensors were prepared in pellet form (10 mm in diameter and 3 mm thick) with a pressure of 7 tons with a Pye–Unicam die. The contacts were made with a silver paste as electrodes on both sides. Figure 1 shows a sketch of the capacitive-type humidity sensor. A Testo 601 capacitive hygrometer was used to monitor the humidity, and a Keithley electrometer was used to measure the resistance.

X-ray diffraction (XRD) studies were performed with a Philips X-ray diffractometer with Cu K $\alpha$  as the radiation source. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a PerkinElmer 1600 spectrophotometer in a KBr medium. The powder morphology of the composites in the form of pellets was investigated with a Philips XL 30 ESEM scanning electron microscope. The temperature-dependent electrical conductivity of the polymer samples was measured with a laboratory-made setup.

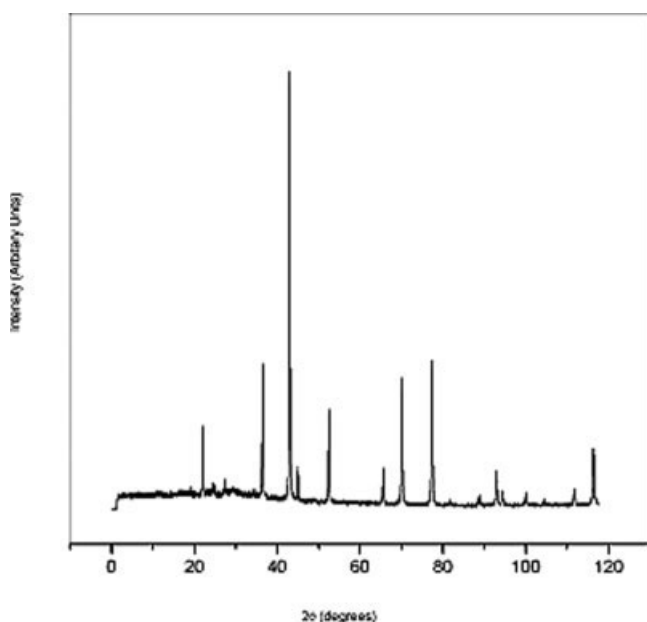
The planar resistance of the sensor was recorded through the control of the humidity in a closed chamber at room temperature. The humidity was first lowered by CaCl<sub>2</sub> being kept in a chamber. Controlled water vapor was then introduced steadily to increase the humidity inside the chamber from 10 to 95% RH. RH inside the chamber was monitored with a standard precalibrated humidity meter.<sup>27,28</sup>

## RESULTS AND DISCUSSION

Figure 2 shows the XRD pattern for the composite having 50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI. The cubic peaks of Co<sub>3</sub>O<sub>4</sub> indicate the crystalline nature of the composite. A comparison of the XRD pattern of the composite with that of Co<sub>3</sub>O<sub>4</sub> (JCPDS) shows that the prominent peaks corresponding to 2  $\theta$  values of 36.75, 43.09, 65.50, 69.90, and 77.54° are due to (3 1 1), (4 0 0), (4 4 0), (5 3 1), and (5 3 3) planes of Co<sub>3</sub>O<sub>4</sub>. The XRD diffraction studies performed on all the samples (10, 20, 30, 40 and 50 wt % Co<sub>3</sub>O<sub>4</sub>) show that the peaks



**Figure 1** Sketch of capacitive-type humidity sensors.



**Figure 2** XRD pattern of the PANI/Co<sub>3</sub>O<sub>4</sub> composite (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI).

are sharp; this is possible because of the formation of oxide particles. By comparing the XRD patterns of the composite and Co<sub>3</sub>O<sub>4</sub>, we have confirmed that Co<sub>3</sub>O<sub>4</sub> has retained its structure even though it is dispersed in PANI during the polymerization reaction.

Figure 3(a,b) shows the FTIR spectra of Co<sub>3</sub>O<sub>4</sub> and PANI–Co<sub>3</sub>O<sub>4</sub> composites (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI). The peaks at 1567, 1485, 1299, 1245, and 1134 cm<sup>-1</sup> confirm the polymerization of aniline and the metal–oxygen stretching frequencies of Co–O at 661 and 568 cm<sup>-1</sup>, as given in Table I. Similar stretching frequencies can also be found in other composites, but the intensity of the metal–oxygen peak increases as the weight percentage of Co<sub>3</sub>O<sub>4</sub> is increased.<sup>29,30</sup> A slight shift in the metal–oxygen stretching frequencies from 662 (pure Co<sub>3</sub>O<sub>4</sub>) to 661 cm<sup>-1</sup> in the composite (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) and from 570 (pure Co<sub>3</sub>O<sub>4</sub>) to 568 cm<sup>-1</sup> in the composite (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) indicates the weak interaction between Co<sub>3</sub>O<sub>4</sub> and PANI.<sup>27,31</sup>

A scanning electron microscopy (SEM) micrograph for 50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI is shown in Figure 4. The composite possess grains and a porous structure. Furthermore, the composites have capillary pores connected by pores. Such composites are likely to facilitate the adsorption of water vapors because of the large surface area and capillary pores. The SEM studies performed on all the samples indicate a transformation from a cluster pattern to a highly branched porous structure with an increase in the weight percentage of Co<sub>3</sub>O<sub>4</sub>.<sup>32</sup>

Figure 5 shows the temperature-dependent conductivity of the PANI/Co<sub>3</sub>O<sub>4</sub> composites (10, 30, and

50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI). The conductivity varies directly with the temperature, obeying an expression of the following form:

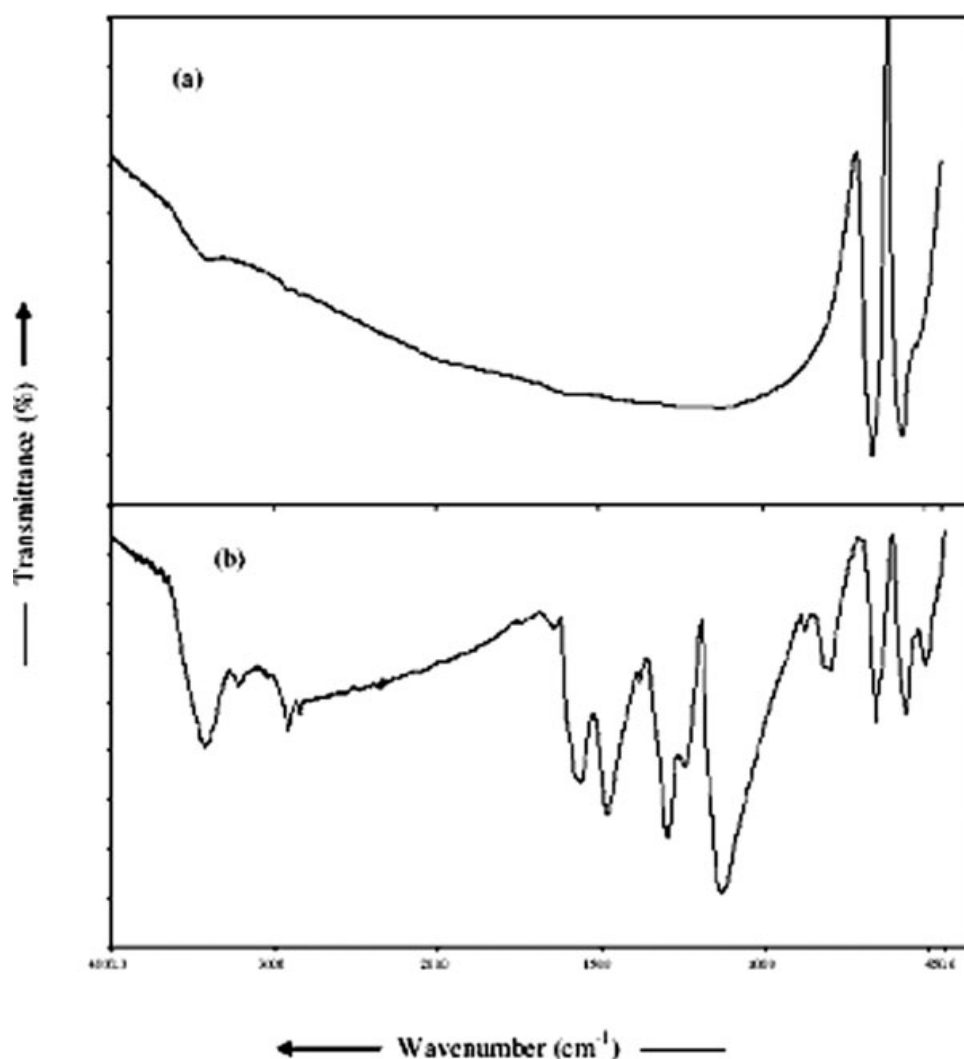
$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (1)$$

where  $\sigma$  is the conductivity,  $T$  is the temperature, and  $\sigma_0$  is the conductivity at characteristic temperature  $T_0$ . Various values of the exponent (e.g.,  $T^{-1/4}$ ,  $T^{-1/3}$ ,  $T^{-1/2}$ , and  $T^{-1}$ ) have been reported, and different models have been used to interpret the data. Also, for the first time, an allometric scaling law for a conductive polymer between the resistance and the section area was proposed by He.<sup>33</sup> The direct-current conductivity of the PANI/Co<sub>3</sub>O<sub>4</sub> composites was obtained by the measurement of the current flowing through the sample and by the use of the sample dimensions to calculate the conductivity with the following equation:

$$\sigma(\text{S/cm}) = \left(\frac{d}{AV}\right)I \quad (2)$$

where  $d$  (cm) is the sample thickness,  $A$  is its area (cm<sup>2</sup>),  $V$  is the potential across the material, and  $I$  is the current flowing across the material. The figure shows that the conductivity increases with increasing temperature. Among the five composites, PANI/Co<sub>3</sub>O<sub>4</sub> (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) was yielded with the highest conductivity. This sudden increase in the conductivity could possibly be explained on the basis of percolation theory. The conductivity increases as the weight percentage of Co<sub>3</sub>O<sub>4</sub> in PANI is increased. The increase in the conductivity with an increase in temperature is a characteristic of thermally activated behavior. The decrease in the resistance or increase in the conductivity may be due to the increase in the efficiency of charge transfer between Co<sub>3</sub>O<sub>4</sub> and polymer chains with an increase in the temperature.<sup>34,35</sup> Moreover, the thermal curing affects the chain alignment of the polymer, which leads to the increased conjugation length and therefore to the increased conductivity. Also, there has to be molecular rearrangement on heating, which makes the molecular conformation favorable for electron delocalization.<sup>36</sup>

Figure 6 shows the characteristic response of the PANI/Co<sub>3</sub>O<sub>4</sub> composites (10, 30, and 50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) as a function of RH. The resistance varies almost linearly from 30 to 95% RH and decreases from low humidity (dry state) to high humidity (wet state). At a low humidity when the adsorption starts on the clean oxide surface, a layer of hydroxyl groups is formed. The water vapor molecules are chemisorbed through a dissociative mechanism by which two surface hydroxyls per water molecule are formed. At higher RH, the water molecules that adsorb on the



**Figure 3** FTIR spectra of (a)  $\text{Co}_3\text{O}_4$  and (b) the PANI/ $\text{Co}_3\text{O}_4$  composite (50 wt %  $\text{Co}_3\text{O}_4$  in PANI).

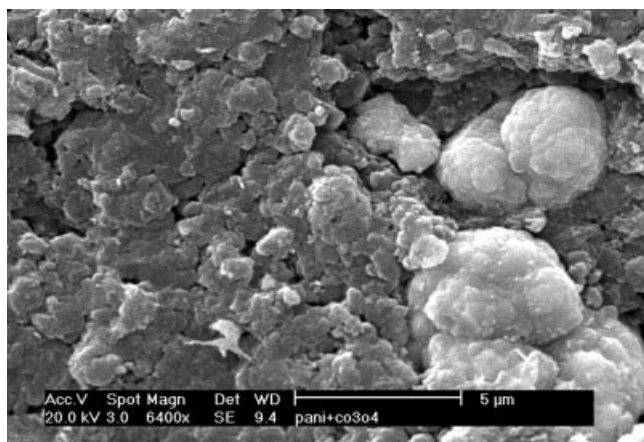
PANI/ $\text{Co}_3\text{O}_4$  composite (50 wt %  $\text{Co}_3\text{O}_4$  in PANI) having grains and capillary pores enhance the electrolytic conduction as well as the protonic conduction by permitting capillary condensation of water molecules within the pores. The response time for sensing a 10% increase in the RH values has been measured to be about 4–5 s; it returns to the normal value in around 10 s. The samples were stable more than 1 year.

The increase in the conductivity or decrease in the resistance with increasing humidity can be attributed

to the mobility of the  $\text{Co}_3\text{O}_4$  ion, which is loosely attached to the polymer chain by weak van der Waals forces of attraction. At a low humidity, the mobility of the  $\text{Co}_3\text{O}_4$  ion is restricted because under dry conditions the polymer chains tend to curl up into a compact, coil form. On the contrary, at a high humidity, the polymer absorbs water molecules, and this is followed by the uncurling of the compact, coil form into straight chains that are aligned with respect to one another. This geometry of the polymer is favorable for

**TABLE I**  
IR Peak Positions of the PANI/ $\text{Co}_3\text{O}_4$  Composite

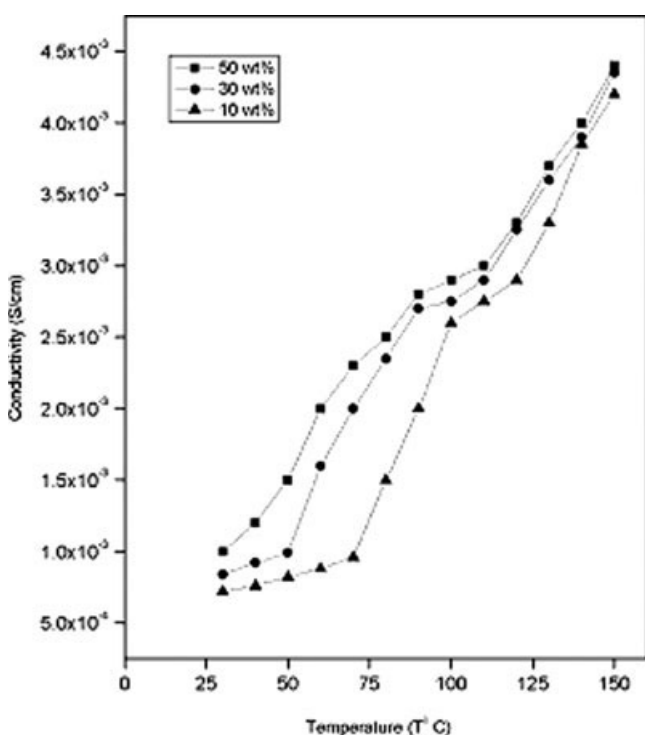
Wave number ( $\text{cm}^{-1}$ )	Component	Assignment
1566	PANI	Ring stretching
1487	PANI	C–N stretching + C–C stretching
1298	PANI	C–N stretching + CH bending
1244	PANI	C–N stretching + C–C stretching
1125	PANI	CH (ipso) bending
661 and 568	PANI and $\text{Co}_3\text{O}_4$	$\nu_{\text{m-o}}$



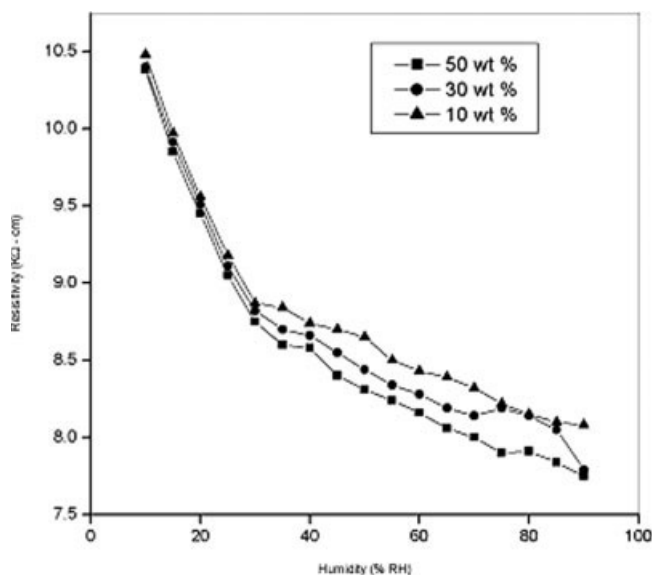
**Figure 4** SEM micrograph of the PANI/Co<sub>3</sub>O<sub>4</sub> composite (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI).

enhanced mobility of the Co<sub>3</sub>O<sub>4</sub> ion or charge transfer across the polymer chains and hence the conductivity.

Also, it has been reported that the conductivity of a conducting polymer increases when the sample absorbs moisture. A reduction of the resistance with an increase in the humidity proves the adsorption of the water molecules, which makes the polymer more *p*-type in nature; that is, the hole concentration is increased by the donation of the lone pair from the conducting complex toward the Co<sub>3</sub>O<sub>4</sub> water molecules. Thus, the partial charge-transfer process of



**Figure 5** Temperature-dependent conductivity of the PANI/Co<sub>3</sub>O<sub>4</sub> composites (10, 30, and 50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI).



**Figure 6** Variation of the resistivity with the change in RH (%) for the PANI/Co<sub>3</sub>O<sub>4</sub> composites (10, 30, and 50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI).

conducting species with that of water molecules results in the decrease in the sheet resistivity. At a higher humidity level, the mechanism may be different. The almost linear variation with respect to RH can be used in an amplifier circuit for converting the measured values into measurable RH values. Careful observation of Figure 6 shows that the PANI/Co<sub>3</sub>O<sub>4</sub> (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) composite has a linear response from 30 to 95% RH. On the other hand, in the PANI/Co<sub>3</sub>O<sub>4</sub> composites (10 and 30 wt % Co<sub>3</sub>O<sub>4</sub> in PANI), the resistance drops from 30 up to 60% RH in a linear fashion, whereas after 60% RH, slight saturation can be observed with a very small decrease in the resistance up to 95% RH. In other words, the PANI/Co<sub>3</sub>O<sub>4</sub> (10 and 30 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) composites show a two-step sensing response. Thus, PANI/Co<sub>3</sub>O<sub>4</sub> (50 wt % Co<sub>3</sub>O<sub>4</sub> in PANI) shows better sensing properties and exhibits good linearity in a sensing response curve.<sup>37</sup>

## CONCLUSIONS

PANI/Co<sub>3</sub>O<sub>4</sub> composites were synthesized by an *in situ* chemical polymerization method with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an oxidizing agent. This was a novel polymerization process for the direct synthesis of the emeraldine salt phase of the polymer. By comparing the XRD patterns of the composite and Co<sub>3</sub>O<sub>4</sub>, we confirmed that Co<sub>3</sub>O<sub>4</sub> retained its structure even when dispersed in PANI during the polymerization reaction. The formation of mixed phases of the polymer together with the conducting emeraldine salt phases was confirmed by spectroscopic techniques. An SEM micrograph revealed the homogeneous distribution of Co<sub>3</sub>O<sub>4</sub> in

the polymer. High-temperature conductivity measurements showed the thermally activated behavior of the composite. The almost linear response of PANI/Co<sub>3</sub>O<sub>4</sub> (50% Co<sub>3</sub>O<sub>4</sub> in PANI) composites to a broad humidity range proved this to be a competent material for humidity sensing.

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