

ELECTRICAL CONDUCTIVITY, DIELECTRIC BEHAVIOR AND HUMIDITY SENSING PROPERTIES OF POLYANILINE-GRAPHITE OXIDE COMPOSITES

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ABSTRACT

Composites of polyaniline (PANI)-graphite oxide (GO) were synthesized by a single-step in-situ chemical polymerization of aniline over fine graded powder of GO. The composite formation and the structural changes were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infra red spectroscopy (FTIR). The DC conductivity of the composite has been investigated within a temperature range from 300 K to 433 K and the temperature dependent conductivity exhibited semiconducting behavior. Room temperature AC conductivity and dielectric behavior of the composites were studied in the low frequency range of 50 Hz to 5 MHz. Variation of AC conductivity obeyed the power law and the dielectric response showed relaxation contribution coupled by electrode polarization effect. Humidity sensing properties of the composites were studied using a self-fabricated sensor set up. The electrical resistance as a function of varying humid environment ranging between 20 and 90 % relative humidity (RH)) is recorded to evaluate the sensitivity of the PANI-GO composite samples towards humidity. The resistance of the samples was found to decrease with increasing humidity due to absorption of water molecules which provides the better conducting paths. Composite with 50 wt% of GO has shown better sensor response than lower loading of GO particles in the polyaniline matrix. Our observations suggest that the PANI-GO composites are potential materials for humidity sensors.

KEYWORDS: Polyaniline, Graphite Oxide, Composites, Conductivity, Humidity Sensing

INTRODUCTION

Intrinsically conducting polymers have been the subject of extensive theoretical and experimental studies for the past few decades. Among the conducting polymers, polyaniline (PANI) is one of the most attractive materials due to its unique electrical properties, environmental stability, easy fabrication process, etc [1,2]. Conducting polymer-inorganic oxide composites formed by the dispersion of inorganic oxide in conducting polymer matrix have received much attention in the past few years [1-3]. These composites are expected to display new properties over their single components, making them potential candidates for application in several fields such as sensors, electromagnetic interference (EMI) shielding, corrosion protection, catalysis, electrode materials for batteries, biosensors, memory devices, etc. Conducting polymer-inorganic oxide composites are considered as heterogeneous disordered systems with a complementary behavior between the matrix phase and the inorganic dispersed phase [4-7].

The sensing and controlling of humidity, one of the most common constituents present in the environment, is of great importance in industrial processes, moisture sensitive products, food storages, hospitals, museum, electronic devices, libraries, environmental protection, meteorology, etc [8-10]. Due to the considerable increase in the demand for humidity

control in various fields, sensors made from inorganic oxides like aluminum oxide, titanium oxide, tin oxide and iron oxide have been emerged as humidity sensors in recent years [11-13]. But, sensors based on inorganic oxides have several limitations like high temperature operation and poor performance with respect to the sensitivity, long term stability, selectivity, etc. Conducting polymers have shown very promising results for sensor applications as they can be used at room temperature and show high sensitivity to gases and humidity due to their porous nature. Due to its interesting properties, polyaniline has been a potential candidate in sensor applications [14,15]. Graphite oxide (GO) has been reported to be potential material for various technological applications. This physically and chemically stable GO has been extensively investigated at both room and elevated temperatures [16-18].

In the present article, we report on the preparation of composites of conducting PANI and graphite oxide by using in-situ chemical polymerization route. The conductivity, dielectric properties and humidity sensing behavior of these composites were studied. The effect of GO concentration on conductivity and dielectric properties were investigated. The humidity sensing characteristics of the composites were measured at room temperature and the improved humidity response of the PANI-GO composite is explained in terms of the synergetic interaction of both PANI and the GO particles. The quick response for changing humidity exhibited by the composites and the linear variation in the parameters indicate the prospects of these composite as an efficient humidity sensing material.

EXPERIMENTAL

All chemicals used were of research grade. The monomer aniline was doubly distilled prior to use. Ammonium peroxydisulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS), hydrochloric acid (HCl), and graphite oxide (Sigma-Aldrich, India) were used as received. Aniline (0.1mol) was dissolved in 1M HCl to form aniline hydrochloride solution. GO was added to the aniline hydrochloride solution with vigorous stirring to keep the GO suspended in the solution. To this reaction mixture, 1M APS, which acts as the oxidant was added drop-wise with continuous stirring at a controlled temperature of 0-5 °C in an ice bath. After complete addition of the oxidizing agent, the reaction mixture was kept stirring for 4hours [1-4]. The resultant precipitate of the polymer composite was washed thoroughly and filtered using acetone and water. The resultant precipitate composite was dried in an oven for 24 hours to achieve a constant weight. Thus, different PANI-GO composites were prepared by in-situ chemical oxidative polymerization of aniline over fine graded graphite oxide with wt % of 10, 20, 30, 40, and 50 (PG10-PANI with 10 wt% of GO, PG20-PANI with 20 wt% of GO, PG30-PANI with 30 wt% of GO, PG40-PANI with 40 wt% of GO, PG50-PANI with 50 wt% of GO). The synthesized composite powder was pressed into circular pellet of diameter 10 mm and thickness 2-2.5 mm for the electrical conductivity and humidity sensing studies.

Surface morphology of PANI, GO and PANI-GO composites were investigated by scanning electron microscopy (SEM) using Philips (model-XL30) ESEM. X-ray diffraction (XRD) was carried out by X-ray powder diffraction at an ambient temperature for the structural characterization of PANI, GO and PANI-GO composites. A Rigaku (model-RU-300) X-ray diffractometer with Cu K_α (1.54\AA) radiation was used. The Fourier transform infrared (FTIR) spectra PANI, GO and PANI-GO composites were recorded on a Perkin-Elmer spectrometer (model-783) in KBr medium.

The temperature dependent DC conductivity was recorded using two probe methods using Keithley-2000 multi meter. The measurements were recorded during cooling cycle. Room temperature AC conductivity and dielectric studies were carried out over the frequency range 50 Hz to 5 MHz, using Hioki LCR meter (model: 3532-50).

The samples in the pellet form were used for humidity sensing. The planar resistance of the sensor was recorded by controlling the humidity in a closed laboratory made glass chamber at room temperature [19,20,21]. The humidity was first lowered by keeping CaCl_2 in the chamber. Controlled water vapors at room temperature were then introduced steadily

for increasing the humidity inside the chamber from 20 to 90% RH. Relative humidity inside the chamber was monitored and measured by a standard pre-calibrated hygrometer (Mextech; model DT-615).

RESULTS AND DISCUSSIONS

Scanning Electron Microscopy

The scanning electron micrograph (SEM) of pure PANI and PANI-GO composite (50 wt% of GO in polyaniline) are shown in Figure 1. The SEM of pristine PANi (Figure 1a) shows the formation of a spongy irregular agglomerated structure [2,4,22]. The SEM studies performed on the composite sample (Figure 1b) reveals the presence of GO particles covered by polyaniline chain agglomerates and the microstructure shows the presence of modified aggregate porous regions which may facilitate electrical, dielectric and humidity sensing response for the composites.

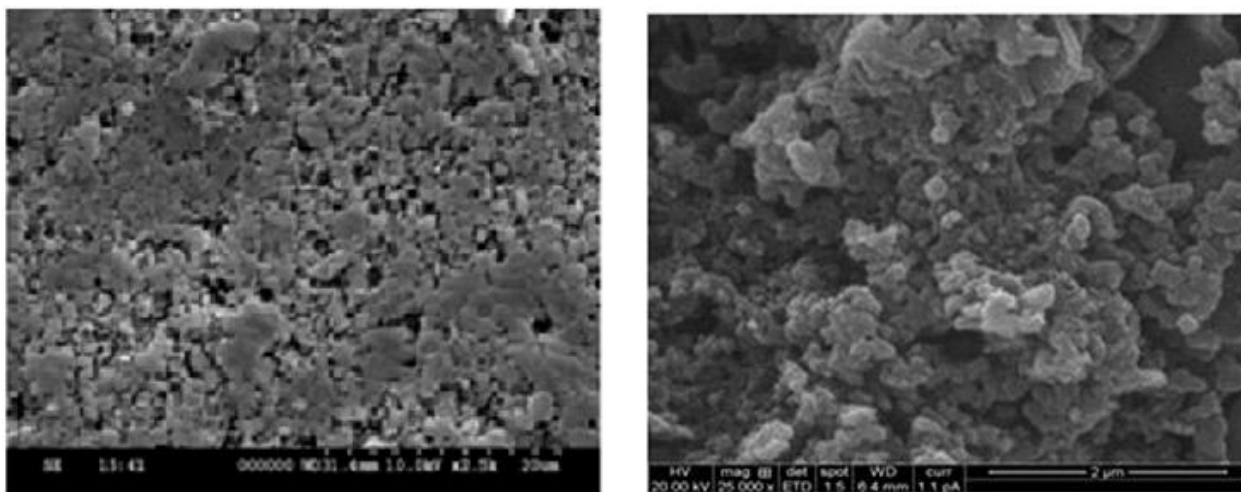


Figure 1: SEM of (a) Pristine PANI and (b) PANI-GO Composite

X-ray Diffraction

Figure 2 shows the X-ray diffraction (XRD) patterns of pristine PANI, GO and PANI-GO composite with 50 wt% of GO in PANI. Careful analysis of X-ray diffraction of polyaniline in Fig.2(a) suggests its semi-crystalline nature with a broad peak centered around $2\theta \approx 26^\circ$ [2,4]. Figure 2(b) represents the XRD pattern of GO. The layered structure of the parent graphite is confirmed by the characteristic peaks between $2\theta = 31^\circ$ to 37° [JCPDS File No. 41-1487]. The XRD pattern of PANI-GO composite (with 50 wt% of GO in PANI) is shown in Figure 2(c). By comparing the XRD patterns of the composite and GO, it is confirmed that GO has retained its structure even though it is dispersed in PANI during polymerization reaction.

Infra Red Spectroscopy

Figure 3 shows the FTIR spectra of PANI, GO and PANI-GO composite with 50 wt% of GO in PANI. Figure 3(a) represents the FTIR spectra of pure polyaniline with prominent peaks around 1400 cm^{-1} to 1600 cm^{-1} results due to the stretching of C=N and C=C of quinoid and benzoid ring [4,22,23]. The broad peaks between 900 cm^{-1} to 1300 cm^{-1} are due to C-N and C-C stretching frequencies [11]. The sharp and prominent peak around 1000 cm^{-1} in the FTIR spectra of GO shown in Figure 3(b) is a characteristic peak for GO ascribed due to C-O bending mode. The -OH stretching frequency and hence the presence of lattice water is shown by the weaker band around 3600 cm^{-1} . Figure 3c, shows the FTIR spectra of PANI-GO composite. All the prominent peaks observed in pure PANI are retained in the composite while the peaks of GO have disappeared. This suggests the binding GO particles with organic PANI matrix. By careful

observation of IR, the characteristic stretching frequencies are considerably shifted towards higher frequency side. The data suggests that, there is a Vander walls kind of interaction between the polymer chain and GO.

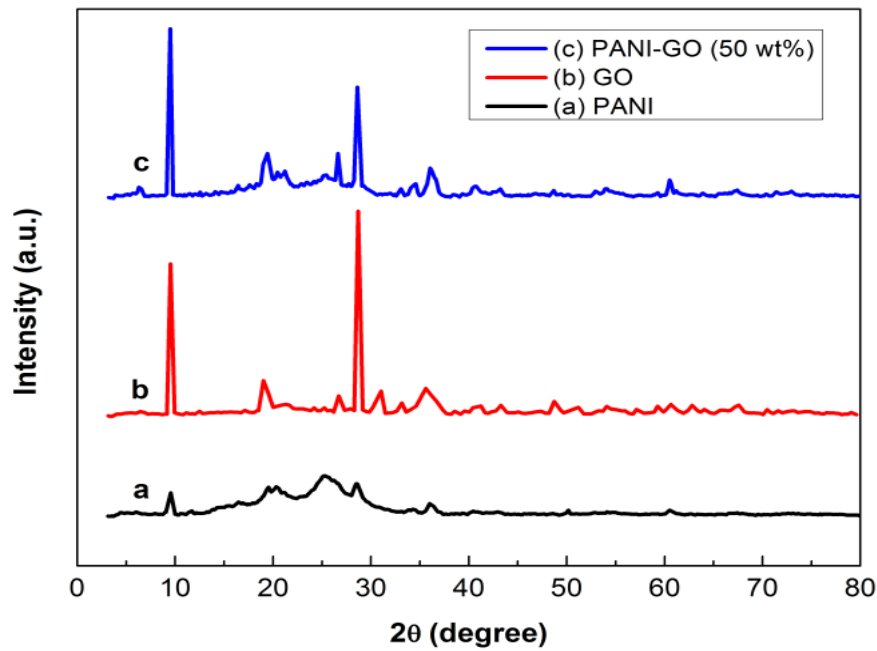


Figure 2: X-ray Diffraction Patterns of (a) PANI, (b) GO, and (c) PANI-GO Composite (PG50)

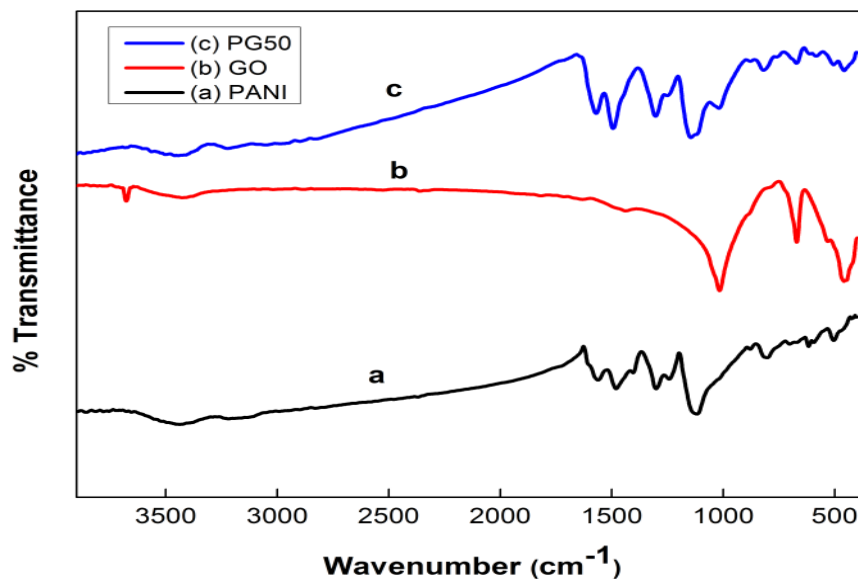


Figure 3: FTIR Spectra of (a) PANI, (b) GO, and (c) PANI-GO Composite

DC Conductivity

The variation in DC conductivity (σ_{dc}) as a function of temperature for PANI-GO composites is shown in Figure 4. With increase in temperature the conductivity σ_{dc} is found to increase. The dc conductivity is seen to be of two phases. The variations in the conductivity values are minimum in the first phase where the temperature range is 35-120 °C. In the second phase, the conductivity increases suddenly for higher temperatures. This indicates typical semiconducting behavior of the PANI-GO composites. The observed conductivity variations are very prominent for the GO composite with 50 wt % of GO in PANI (PG50). The DC conductivity behavior of the composites may be attributed to the thermally assisted hopping of polarons from one localized state to another, that can be confirmed by Mott theory [24,25-27]. The variation in

distribution of GO particles in PANI matrix favors more number of charge carriers to hop between favorable localized sites causing increase in conductivity. Variation of DC conductivity as a function of wt% of GO in PANI at three fixed temperatures viz., at 40, 80 and 120°C is shown in figure 5. It is observed from the figure that with increasing content of GO in PANI, the DC conductivity increases. Increasing content of GO in PANI results in the formation of more number of conducting islands and a strong coupling interactions between PANI chain and GO particles.

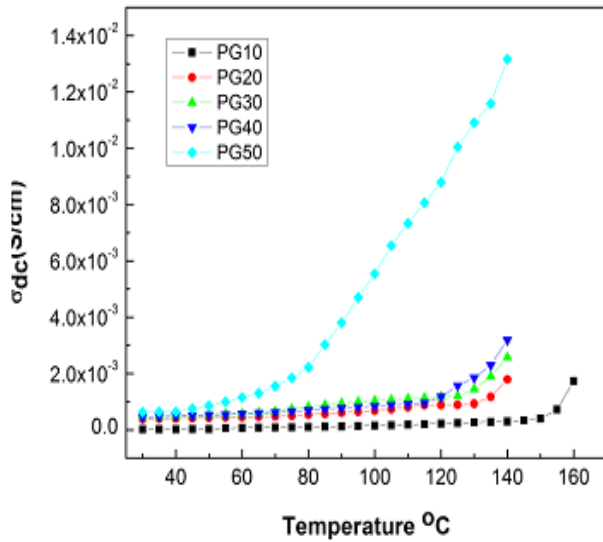


Figure 4: Variation of σ_{dc} as a Function of Temperature for PANI-GO Composites

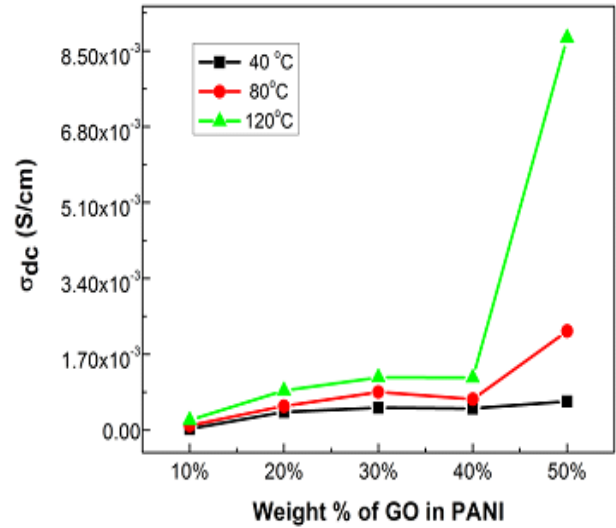


Figure 5: Variation of dc Conductivity with Concentration of GO

Low Frequency AC Conductivity

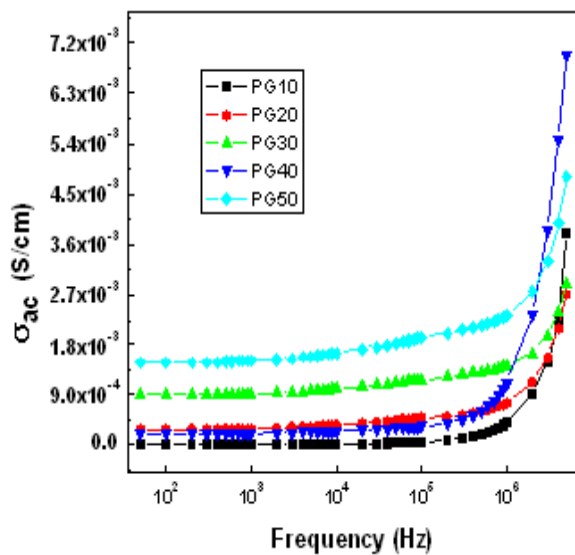


Figure 6: Low Frequency AC Conductivity of PANI-GO Composites

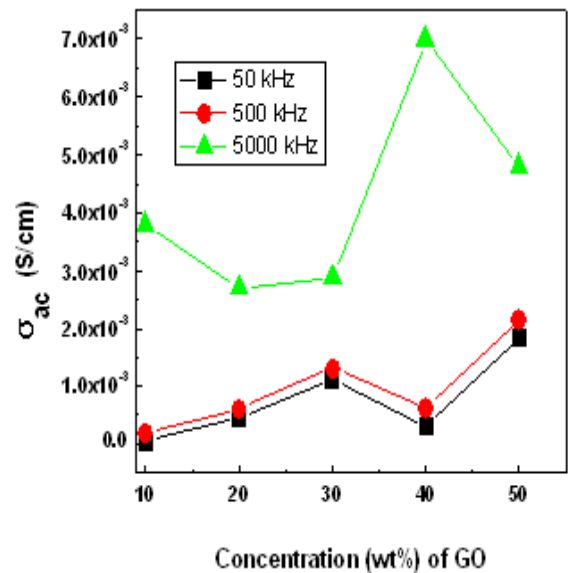


Figure 7: Variation of AC Conductivity (σ_{ac}) as a Function of wt% of GO in PANI

Low frequency AC conductivity of PANI-GO composites is shown in Fig.6. The σ_{ac} of all the composite samples exhibits a frequency independent conductivity up to 100 kHz and then increases sharply thereafter. The AC conductivity increased with increasing concentration of GO in PANI and was found to be maximum in PG50 composite. The frequency independent region followed by a high frequency dispersed region in these PANI-GO composites follows the universal behavior of frequency dependent conductivity in disordered media [4, 28, 29]. The AC conductivity component contributing to the dispersive region in the high frequency is described by Jonscher's universal law, $\sigma_{ac} \propto \omega^n$ [30], where n

is a fractional exponent roughly treated as constant (less than 1). At higher frequencies, conductivity increases due to inter chain and intra chain hopping of charge carriers (polaron/bipolaron). The observed conductivity variation is also attributed to the variations in the charge flow along the various clusters of the PANI coated GO composites.

The electrical conductivity studies are significantly relevant for assessing the electronic properties and various technological applications of these composites. Figure 7 shows the variation of AC conductivity as a function of concentration (wt %) of the dispersant GO in PANI at three selected frequencies (50 kHz, 500 kHz, and 5000 kHz). Among the various PANI-GO composites, there was a marginal increase in the conductivity up to 50 wt% with a minimal variation at 40 wt%.

The observed marginal variations are attributed to the heterogeneity of these composites in the presence of GO leading to morphological modifications [31]. The modified morphological features of the PANI matrix in the presence of GO can facilitate various distinct functional properties. The obtained results indicate that, the higher wt% of GO in PANI matrix are expected to provide better conductivity.

Dielectric Properties

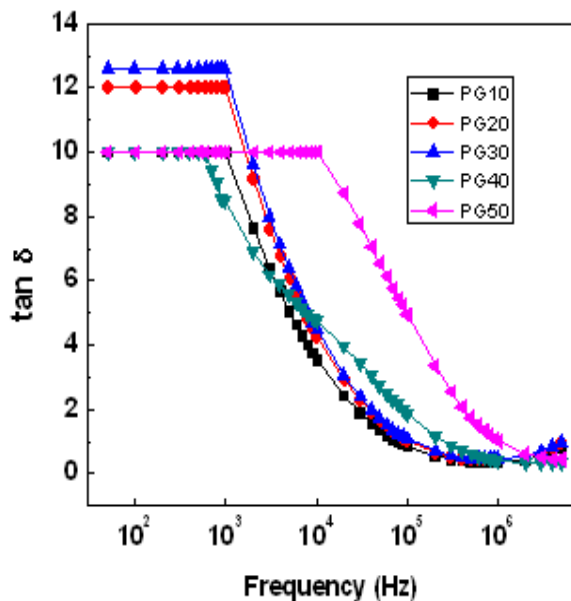


Figure 8: Variation of Dielectric Loss as a Function of Frequency for PG Samples

Figure 8 shows the variation of dielectric loss of the PANI-GO composites as a function of frequency. It is observed that the dielectric loss tangent decreased with increasing frequency. The observed dielectric loss values of the composite samples show frequency independent behavior up to 1kHz for lower concentrations of the PANI-GO composites (up to 40 wt%), whereas for 50 wt% concentration of PANI-GO composite, the dielectric loss was constant up to 10 kHz. The variations of $\tan \delta$ values are in accordance with the observed conductivity response of these composites.

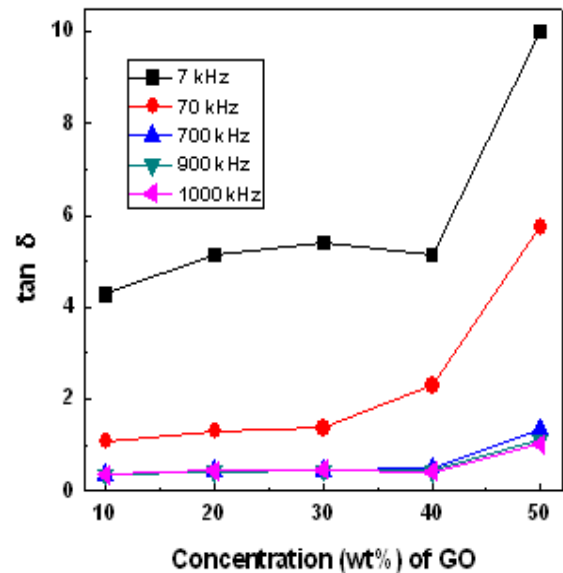


Figure 9: Variation of Dielectric Loss ($\tan \delta$) as a Function of wt% of GO in PANI

The composites of PANI with GO exhibit modified electrical properties and lead to various relaxation phenomena in the disordered semiconducting system. The variations in the dielectric loss as a function of GO concentration in PANI matrix is shown in Figure 9. The observed variation is similar to the DC conductivity and AC conductivity properties. This behavior is in agreement with that reported in the literature [4, 32-34].

Humidity Sensing Properties

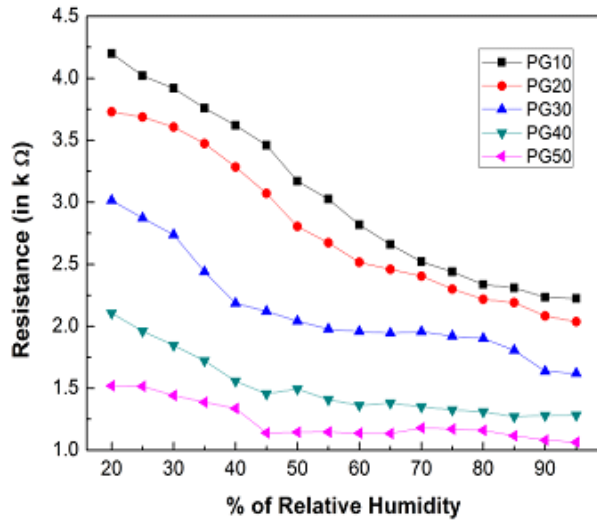


Figure 10: Resistance as a Function of Relative Humidity (RH) Value for PANI-GO Composites

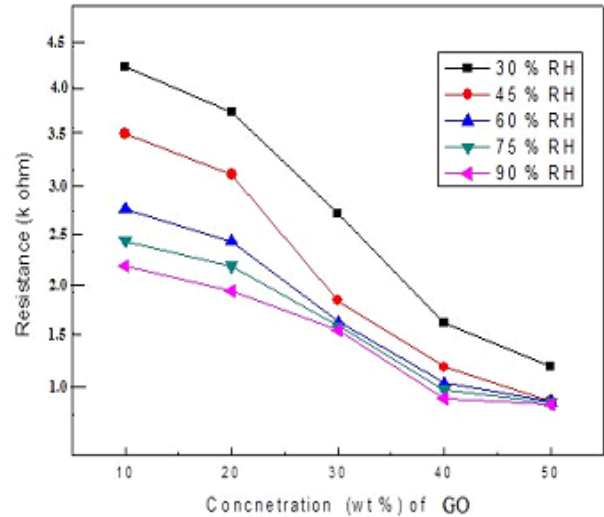


Figure 11: Variation of Resistance with wt% of GO in PANI at Selected Relative Humidity

Figure 10 shows the change in the resistance of PANI /GO composites with increase in percentage relative humidity. In all the composites the resistance was found to decrease with increase in relative humidity. The change in resistance was observed to be significant with increasing content of GO in PANI. The change in resistance of the composites is due to absorption of humidity which causes swelling of polymer chain as well as trapping of water molecule in the voids formed in between the polymer and GO particles. The decrease in resistance is also due to adsorption of water molecules by the pellet surface. Typically on exposure to water vapor, polyaniline becomes protonated, and an increase in conductivity is observed. The humidity sensing property of polyaniline to water vapor can be regarded as electron hopping assisted by proton transfer mechanism and capillary condensation of water molecules into the sample surface [35]. At low humidity, the trapping of the water molecules is less therefore the polymer chains would tend to curl up into compact coil form. On the contrary, at high humidity, the polymer absorbs water molecules, and polymer chains swells, followed by the uncurling of the compact coil and forms into straight chains that are aligned with respect to each other. Figure 11 shows the variation of resistance with concentration of (wt%) GO in PANI for five fixed relative humidity of 30, 45, 60, 75 & 90 % RH. With increase in weight percent of GO in PANI, the resistance was found to decrease. This could be due to an increase in the heterogeneity of the composite with increasing amount of GO which is also seen from SEM. All the PANI-GO composites have shown better response towards humidity sensing and the composite with 50 wt% of GO in PANI shows significant reduction in resistance, indicating its potential as a polymer based humidity sensor.

CONCLUSIONS

In this study, electrical conductivity, dielectric behavior and humidity sensing properties of synthesized polyaniline-GO composites were investigated. The scanning electron micrograph of the composites show modified morphological features with heterogeneous aggregate structures which are suitable for humidity sensing applications. X-ray diffraction studies show the retention of structure by GO particles in polymer matrix. Formation of PANI/GO composites was observed from FTIR studies. The electrical properties in these composites show a strong dependence on content of GO in PANI matrix. Change in resistance in the composites was observed with change in humidity. With increase in humidity, maximum decrease in resistance was observed in composite with 50 wt% of GO in PANI. Hence this composite is a promising material for humidity sensing applications.

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