Research Article

Microarticstructural, Spectroscopic, and Magnetic Analysis of Multiwalled Carbon Nanotubes Embedded in Poly(o-aminophenol) Matrices

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1. Introduction

One of the most important materials for energy storage and environmentally friendly technology is conducting polymers. Due to their iconic properties, they can be used in a vast range of applications including corrosion inhibitors, solar cells, sensors, batteries, microelectronics, and electrochromic devices. [1–4] Carbon nanotubes, because of their conductivity, nanostructure, and resilience, are used in different electrochemical applications, especially supercapacitors. The performance of supercapacitors depends upon the accumulation of charge at the electrode/electrolyte interface [5–8]. A pure CNT acts as a moderate capacitor. It has been found that a thin amorphous layer on the walls of CNT enhances its charge accumulation capacity [9]. Hence, MWCNTs can play a flawless role in active materials such as conducting polymers for supercapacitor applications. Among the conducting polymers, poly-ortho-aminophenol is of great interest because of its highly stable nature, high conductivity, flexibility to doping, and better redox reversibility [10].

In the recent past, conducting polymer nanostructures, such as polypyrrole and polyaniline, have been developed and well studied [11–18]. The most fascinating members of the substituted aniline family are aminophenols. The phenyl ring’s hydroxyl group may be oxidised to quinine, which can then be reduced again. When electropolymerized in an alkaline solution, PoAP surfaces have electrochemical and electrochromic properties. As a result, various anilines and substituted anilines have two oxidizable groups (-NH₂ and -OH). The family position of the amino and hydroxyl groups in the aromatic ring is a crucial sequence.
Chemical stability, convenient surface area, particular structure, restricted dispersion magnitude, and low resistivity are all features of multiwalled carbon nanotubes (MWCNTs). CNTs’ large surface area and conductivity may help conducting polymers enhance their redox characteristics [19–21]. The creation of a charge-transfer complex between MWCNTs in the composites and the weak Van der Waal contacts between them promotes MWCNT dispersion within the PoAP matrix, resulting in improved electrical conductivity. MWCNTs, on the other hand, lose their orientation when they are randomly scattered in a polymeric matrix. Nanotube-polymer composites are projected to have a significant anisotropy due to their unique one-dimensional structure [22]. Another effective approach for aligning carbon nanotubes in a polymeric matrix is to use a magnetic field. In aligned CNTs, all properties enhance significantly in comparison to the randomly oriented CNTS in the polymer matrix. We have previously described that cobalt chloride was the superlative dopant for PoAP than added inorganic matrix. We have previously described that cobalt chloride comparison to the randomly oriented CNTS in the polymer matrix. We have previously described that cobalt chloride was the superlative dopant for PoAP than added inorganic acid, thus, thenanocomposite pellets were doped with cobalt chloride and CoCl₂ acids doping with an excellent magnetism effect of PoAP & PoAP/MWCNT/f-MWCNT nanocomposites are commonly used as the reinforcement phase due to their high strength [11].

In this work, we report a detailed study on conducting polymer nanocomposites utilizing MWCNT and functionalyzed MWCNT (-COOH) with PoAP. Using in-situ chemical polymerization of o-aminophenol in an aqueous sodium hydroxide (NaOH) medium with varying wt percent MWCNT concentration, the nanocomposite of PoAP-MWCNT and MWCNT (-COOH) was produced. Different characterisation approaches were used to examine the structural morphology and conductivity of PoAP/MWCNT and MWCNT (-COOH). More importantly, CoCl₂-per- suaded doping interaction of pure PoAP with MWCNTS was explained based on spectral, thermal, and magnetic properties. The Co-doped PoAP/MWCNT and MWCNT (-COOH) have been used as a precursor for Co nanoparticles by the thermal decomposition route; we have tried to establish the fact that PoAP/MWCNT and MWCNT (-COOH) composite insinuations in crystal engineering and design for numerous applications, which is supported by conductivity measurements in the presence of magnetic fields. The conductivity of the composite reacts differently in parallel and antiparallel magnetic fields.

2. Materials and Methodology

Ortho aminophenol and functionalized multiwalled CNT [-COOH] & pristine MWCNT (95% purification, diameter = 10–15 nm, length = 0.1–10 μm, density = 1.7–2.1 g/cm³) were purchased from Sigma–Aldrich. Other reagents such as ammonium persulfate (APS) (Merck, India) were of analytical grade. Sulfuric acid and cobalt chloride (Merck, India), hydrochloric acid (S. D. Fine Chemicals, India), DMSO (Merck, India), N-N-dimethyl formamide (DMF) (Merck, India), and acetonitrile (Merck, India) were employed without additional purification. For synthesis and washing, deionized water was employed.

Poly (o-aminophenol) (PoAP) was prepared by oxidative polymerization of o-aminophenol (o-AP) in an alkaline medium with NaOH (with 0.6 M concentration). At room temperature, APS (0.045 M, 10.26 g) was added to the solution of oAP in two-necked round bottom flasks. The aqueous APS solution was added auxiliary dropwise to the basic oAP solution using a dropping funnel for 1 h. The reaction vessel was retained on an ice bath and the temperature was sustained at 3°C throughout the reaction extent. Then, 0.7–0.8 g of PoAP and PoAP/MWCNT/f-MWCNT (3 wt%) were dissolved in 10–15 ml DMSO. Later, this solution was transferred to a Petri dish with a diameter of 10 cm. The solution was heated at 100°C for 7–8 hrs. in an oven. A dark-tinted powder was formed once the solvent was completely evaporated. Furthermore, the polymer powder was vacuum filtered after being dipped four–five times alternatively in deionized water and acetonitrile to remove the retained DMSO. Following adequate drying, the sample powder was pressed for approximately 5 minutes in a mould using a hydraulic press (Model PTB-920) with 6 tons of force to generate disc pellets, which were subsequently utilized for characterisation.

FTIR spectra of the nanocomposite samples were measured using a Nicolet NEXUS 670 spectrophotometer within the wavenumber array of 3500–600 cm⁻¹. The samples were mixed with KBr (Aldrich, 99%, FT-IR grade) and pelletized. The UV-visible spectroscopic study was carried out for DMSO dispersion of functionalized MWCNTs, pure PoAP, PoAP/f-MWCNT, and PoAP/MWCNT nanocomposite samples. The room temperature Raman spectra were recorded using a RENISHAW in- through Raman microscope with four standard Leica microscope objective lenses in backscattering geometry. The base was an argon ion laser with a 514 nm excitation wavelength. With a 20 s data point acquisition time, the spectra for the range of 400–2500 cm⁻¹ were produced utilizing 2400 lines per millimetre discordant. The surface morphology was studied using scanning electron micro copy (SEM, JEOL JSM model 6390LV) with an accelerating voltage of 15 kV. Thermogravimetric analysis (TGA) was carried out using an NETZSCHTG209 F1 analyzer. The samples were placed in a nitrogen atmosphere and heated up to 700°C with a heating rate of 10°C/min. Impedance characteristics were measured using the HIOKI Hi tester LCR meter (3532-50) in the frequency range of 42 Hz–5 MHz. The M-H curves were measured using a physical property measurement system (PPMS; DynaCool, Quantum Design) in an external magnetic field swept from 70 kOe to −70 kOe and back at different temperatures (from 300 K to 1.9 K). The recorded M-H loops were corrected for the diamagnetic contribution from the brass sample holder used for holding the samples.

3. Results and Discussions

The FTIR analysis was used in this work to track the physical changes in carbon nanotubes following surface treatment. Figure 1 shows the FTIR spectra of pure PoAP, PoAP-functionalized MWCNT, and carboxyl-functionalized
MWCNT/poly-ortho-aminophenol (MWCNTs/PoAP) nanocomposite films. In the spectrum of PoAP, the peaks observed at 3380 and 1602 cm$^{-1}$ are related to the explicit bands of the N–H stretching vibrations and the axial stretching of the C=O groups. The stretching of C–H and C=C groups is attributed to the peak in the region of 1400–1600 cm$^{-1}$. The peak at 1384 cm$^{-1}$ might be attributed to the C=N stretching vibration of a secondary aromatic amine. The band at 1121 cm$^{-1}$ is identified as the C–O–C bond stretching, which confirms the interaction of o-aminophenol with PoAP. The primary peaks of the PoAP spectra are similar, however, the intensity varies. These repercussions may result in PoAP having a distinct morphology.

In comparison with the pristine MWCNTs, carboxyl-functionalized MWCNTs showed additional absorption bands at 1727, 1176, and 1029 cm$^{-1}$, which were externally comparable to the stretching vibrations of carboxylic acid (-COOH) groups [21–23]. The active phonon mode of MWCNTs is ascribed to the FTIR band approximately at 1580 cm$^{-1}$. The excellent results show that the acid combination chemical treatment effectively created carboxyl groups on the ‘MWCNTs’ ends and sidewalls. The free oxygen atoms released by strong acids reacted with the unsteady carbon atoms on the surface of MWCNTs to form carboxylic acid (-COOH) groups in the current surface utilization process. The carboxylic acid (-COOH) groups increased the surface polarity of MWCNTs and were necessary to activate the polymer-MWCNT interaction.

The asymmetrical and symmetrical N–H stretching vibrations have two peaks at 3378 cm$^{-1}$ and 3311 cm$^{-1}$, the characteristic bands of the C=O stretching vibration mode for benzenoid rings have two peaks at 1510 cm$^{-1}$ and 1473 cm$^{-1}$, and the bands at 1401 cm$^{-1}$ and 1220 cm$^{-1}$ can be attributed to the C–O–H deformation vibration and the C–O stretching vibration, respectively. In the presence of a surfactant and MWCNT, PoAP/MWCNT was produced. Due to the unique bands of the N–H stretching vibrations and the axial stretching of the C=O groups in the PoAP structure, the band of PoAP has two peaks at 3380 cm$^{-1}$ and 1602 cm$^{-1}$. The stretching of C–H and C=C groups is identified at peaks in the 1400–1600 cm$^{-1}$ range. The peak at 1384 cm$^{-1}$ might be attributed to a secondary aromatic amine’s C–N stretching vibration. The elongation of the C–O–C links and advanced supply of o-aminophenol different from PoAP are responsible for the peaks at 1121 cm$^{-1}$ [22–24]. The primary peaks of the PoAP/MWCNT spectrum are identical to those of the PoAP shape, but with differing intensities, and it is generally known that the bands of the original MWCNTs are quite faint. These findings show that the MWCNTs have been evenly distributed throughout the polymer matrix.

Figure 2 illustrates the Raman spectra of pure PoAP, PoAP/MWCNT, and PoAP/f-MWCNT nanocomposites. The Raman spectra is for structural imperfections or sp$^3$-carbon in the hexagonal framework of the nanotube walls and first order scattering of the $E_{2g}$ vibration mode in the graphite sheets, respectively [24]. To determine the ratio of sp$^3$-carbon atoms (disordered carbon) to sp$^2$-carbon atoms (graphitic carbon) on the nanotube surface, one must know the relative intensities of these bands. Raman analysis has shown that the f-MWCNT is much greater than the pristine MWCNT, suggesting that the oxidation with the acid mixture might produce a significant amount of covalent functionalization on the surface of the MWCNT. The higher order of surface functionalization on the f-MWCNTs could increase the nanocomposite’s sensitivity.

As perceived in the PoAP/f-MWCNT nanocomposite’s spectrum, the quinoid unit’s C–C ring stretching, C=N stretching, and C-H in-plane bending are all signed by characteristic Raman peaks at 1658, 1560, and 1163 cm$^{-1}$. The C=N stretching vibration of the quinone/polaronic form is attributed to the peak at 1266 cm$^{-1}$. The stretching mode of the C=N polaron radical cation (C=N$^+$), which is a characteristic of the protonated imine form of polymer, is linked to the peak at 1330 cm$^{-1}$, which is located in polymer poly ortho amino phenol (PoAP) [23, 24]. When compared to pure poly-ortho-aminophenol, the Raman band peaks for PoAP/f-MWCNT nanocomposite moved toward higher frequencies and showed a considerable increase in relative intensities (PoAP). For instance, the peak location of the C-N+ stretching is shifted. This finding could be described by the fabrication of a more conductive PoAP matrix with a rich polaronic structure as a result of the electrostatic
interaction between the C-N⁺ groups in the PoAP backbone and the COO⁻ groups of the f-MWCNTs.

To evaluate the interfacial interaction between PoAP and functionalized MWCNTs, UV-visible spectroscopy was used. The UV-vis spectra of pure PoAP, PoAP/MWCNT, and PoAP/f-MWCNT nanocomposites are shown in Figure 3. The PoAP has discrete bands at 225, 380, and 508 nm, which correspond to π−π⁺, polaron−∗, polaron−∗, and π−polaron transitions, respectively. The absorption spectra of pure PoAP unveiled two distinctive bands at ∼400 nm (red shifted) and ∼508 nm, which are connected with π−π⁺ and π−polaron transitions, separately [25].

In the synthesised PoAP-MWCNT and PoAP/f-MWCNT nanocomposites, charge transfer interactions between the PoAP layer and MWCNTs provide evidence for the induced doping. The UV-vis spectra of the monomer ortho-aminophenol (o-AP) and MWCNT arrangement in the reaction media provides resilient for the type of charge transfer complex that was indeed produced in the polymerization medium. The donor [-O⁻] or loa pair on N of (o-AP) was strongly linked with the acceptor MWCNT by major charge transfer in the aqueous NaOH medium. This was sustained by the transition maxima’s red shift to 400 nm for o-AP/MWCNT from 380 nm for o-AP in a NaOH medium in the UV-vis spectrum.

However, three diverse absorption peaks at around ∼302, 425, and 867 nm are perceived in the delocalization diagram for the nanocomposite. In the spectrum of PoAP/MWCNT and PoAP/f-MWCNT nanocomposites, an additional absorption peak at about 425 nm is most likely due to the doping convinced electronic state caused by communication between PoAP imine sites and carboxyl groups in MWCNTs [26, 27]. In addition, this band position is chosen to contrast with the f-MWCNT seen in nanocomposites, which indicates the possibility of interaction between PoAP’s quinoid rings and functionalized multiwall carbon nanotubes (MWCNTs). As a result, the extra molecular connections between the PoAP layer and functionalized MWCNTs in the produced PoAP/MWCNT and PoAP/f-MWCNT nanocomposites are confirmed by UV–VIS spectrum data. The UV absorbance at 380 nm is strengthened, while the absorption at 508 nm is displaced due to the polaron transition. This outcome indicates that PoAP and MWCNT/f-MWCNT nanocomposites can communicate for a long time.

Figures 4–4(d) show the microstructural images of the pure PoAP band, PoAP/MWCNT, and PoAP/f-MWCNT composite films. Although, the surface morphologies of MWCNT and f-MWCNT are shown in Figures 4(e) and 4(f). It can be clearly observed that the morphological features of PoAP/MWCNT nanocomposites consist of porous structures. Interestingly, rod-shaped growth was observed with no porosity in the nanocomposite after functionalization of MWCNTs (e.g., PoAP/f-MWCNT).

Thermogravimetric analysis of the PoAP and PoAP/MWCNT composites are demonstrated in Figure 5. It is observed that all samples show a similar decomposition trend and regular weight loss in three steps. The first weight loss step shows the TGA traces of PoAP and PoAP-MWCNT/f-MWCNT nanocomposites. An initial 7-8% weight loss for all sections up to 110°C could be due to the release of certain water molecules present in the nanocomposite. Up to 220°C, 18% weight loss in TGA is observed for the PoAP. However, the weight loss for PoAP-MWCNT and PoAP/f-MWCNT samples is slightly decreased with 3 wt% of f-MWCNT. This is due to the decaying of some residual products, which might be oxygen (O₂) and water (H₂O) molecules, and this temperature is improved as the 3 wt% of MWCNT & f-MWCNT are increased for enhanced thermal stability. Since the thermal stability of the nanocomposite is higher than the pure polymer, which could be associated...
with the thermal stability of MWCNT. The residual mass left at 750°C was initiated to be 9–21% for the polymer and nanocomposite, separately. The enhanced thermal stability should be ascribed to the interaction between MWCNT & f-MWCNT and copolymer chains. The improvement in composite thermal stability can be explained by the fact that dispersed MWCNTs in polymer nanocomposites can act as physical barriers, slowing decomposition and preventing the diffusion of volatile decayed products out of the polymer nanocomposites, resulting in improved composite thermal stability [28].

Figures 6(a) & 6(b) show the M-H characteristics of PoAP/f-MWCNT and PoAP/MWCNT nanocomposites, respectively. The magnetic parameters obtained from the M-H loop analysis are summarized in Table 1. The absolute values of the exchange bias field (Hex) and coercive field (Hc) are calculated using the formula $H_{ex} = |H_1 + H_2/2|$ and $H_c = |H_1 - H_2/2|$, where $H_1$ and $H_2$ are values of the magnetic field on positive and negative field axes, respectively.

It can be seen that the magnetization of both samples (measured at 300 K and 77 K) rises with the growth in the magnetic field and does not achieve saturation even up to the maximum applied field of 80 kOe. However, the nature seems to be saturated with a mixed phase of ferromagnetic and nearly superparamagnetic behavior at the measured temperature of 1.9 K. This observation can be understood due to the surface spin disorder and canting of spins due to higher thermal energy activation energy at higher temperatures. It can also be noticed from the graph that the
magnetization value increases nonlinearly with the measured temperatures (from 300 K to 1.9 K), which could be because of the interparticle interaction or exchange and dipolar interactions mediated by the polymer matrix [29]. Moreover, the magnetization data is observed to decrease for the functionalized MWCNT sample (at all measured temperatures), which might be due to the interaction of the functional group mediated by other particles being restricted as well as the thermal energy not being strong enough to orient the canted spins (Figure 6(a)). Interactions among magnetic Co particles in MWCNTs may be dispersed in a polymer matrix to become effective enough to restrain the motion of the magnetic moments of the particles at low temperatures.

From Table 1, it is also clear that the value of the coercive field (\(H_c\)) is decreasing along with the decrease in exchange bias from 300 to 1.9 K. The presence of an exchange bias field suggests that a core-shell-like structure (at the interface of the doped MWCNT and PoAP polymer matrix) of the ferromagnetic-antiferromagnetic interface is formed in the sample. Because particle proximity has a significant impact on hysteresis behaviour, they either become more exchange linked or show magnetostatic interactions when the distance between them decreases [30, 31]. Consequently, the decreasing trend in coercivity and increasing trend in the magnetization value with lowering of temperature for the nanocomposite samples suggest that the hysteresis behavior is being changed from ferromagnetic to nearly superparamagnetic. Moreover, the results seem interesting to us and it needs further investigation to shed more light on the magnetic behavior of polymer composites containing carbon nanotubes.

Nyquist plots of the prepared PoAP/f-MWCNT [--COOH] & PoAP/MWCNT nanocomposites are depicted in Figure 7. At a high frequency, a depressed semicircle was seen, followed by a slight spike at a low frequency. The acquired character of the Nyquist plot is typically related to the comparable circuit illustrated in the inset of the illustration. The analogous circuit is made up of a parallel combination of bulk resistance (\(R_b\)) and a constant phase element (CPE1), followed by a series grouping of an additional constant phase element CPE2. CPE1, rather than a capacitor, defines the apparent depression of the Nyquist semicircle, while CPE2 accounts for the development at lower frequencies. The parallel resistor symbolises the ion mobility inside the polymer matrix in a comparable circuit, whereas, the capacitor represents the stationary polymer chain circuit network [32]. A low frequency, a small spike suggests double layer capacitance.

Table 1: The measured magnetic parameters for the polymer nanocomposite samples.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Coercivity (Oe)</th>
<th>Exchange bias (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.9 K</td>
<td>77 K</td>
</tr>
<tr>
<td>PoAP/f-MWCNT</td>
<td>190.5</td>
<td>629.5</td>
</tr>
<tr>
<td>PoAP/MWCNT</td>
<td>91</td>
<td>708.5</td>
</tr>
</tbody>
</table>

Figure 6: M-H characteristics of Co-doped PoAP/MWCNT (3 wt%) and PoAP/f-MWCNT (3 wt%) nanocomposites. Insets show the expanded view of the M-H loop.
due to space charge polarisation and high charge transfer resistance at the electrode/electrolyte interface.

4. Conclusions

In summary, we have successfully synthesised multiwalled carbon nanotubes/poly-ortho-aminophenol (MWCNTs/PoAP) nanocomposite films via the in-situ oxidative polymerization method. The fabricated nanocomposite has shown good thermal stability. A strong interaction has been observed at the interface of PoAP and MWCNT/MWCNT(-COOH), which further leads to the strengthening of UV absorption of PoAP and thereby leading to the blue shift of the π-polaron absorption of PoAP. A magnetic study of Co-doped MWCNTs/PoAP nanocomposites has shown a significant reduction in hysteresis, indicating significant hole doping associated to the oxygen functional groups on the surface of the oxidised carbon nanotube. Magnetization data has been observed to decrease for the functionalized MWCNT sample (Co : PoAP/f-MWCNT), suggesting that the interaction of the functional groups mediated by the polymer matrix is restricted and the thermal energy is not strong enough to orient the canted spins. Moreover, with the lowering of temperature, the nature of the hysteresis curve changed from ferromagnetic to superparamagnetic with a significant exchange bias.

Data Availability

The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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