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Physi-co-chemical Studies on Nano composites of Conducting Polymer using Carbon Nanotubes

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Abstract: Conducting polyaniline (PANI) and its composites were synthesized with different concentrations of multiwall carbon nanotubes (MWCNTs), and their formation was characterized using different characterizing tools. XRD and SEM reveal the homogeneous coating of PANI onto the MWCNT indicating that carbon nanotubes were well dispersed in polymer matrix. The interaction between the Quinoid ring of PANI and the MWCNT causes PANI chains to be adsorbed at the surface of MWCNT, thus forming a tubular core surrounding the MWCNT was confirmed from FTIR. The electrical conductivity of the PANI-MWCNT nanocomposite was higher than pure-PANI increased by increasing the amount of MWCNT to the nanocomposite.

Keywords: Polyaniline, MWCNT, Composites, Electrical conductivity.

I. INTRODUCTION

The combination of carbon nanotubes (CNTs) with insulating or conducting polymers offers an attractive route to reinforce macromolecular compounds, as well as to introduce new electronic properties based on morphological modifications or electronic interactions between the two constituents **[1-2]**. The unique properties of these various types of nanomaterials provide novel electrical, catalytic, magnetic, mechanical, thermal, and other features that are desirable for applications in commercial, medical, military, and environmental sectors**[3,4-7]**. Besides the expected improvements in the mechanical and electronic properties of polymers, the preparation of carbon nanotube/polymer composites has been and is still explored for effective incorporation of CNTs into devices. Nevertheless, the use of CNTs as a rough material in different applications has been largely limited by their poor processability, insolubility, and infusibility. To bypass this disadvantage, an efficient key is the functionalization of CNTs with polymers, **[8]**leading to soluble composite materials. Researchers have been focusing on two types of materials: on one hand, composites based on insulating polymers (IPs) such as polystyrene (PS) or poly (methyl methacrylate) (PMMA), and on the other hand, those made with conducting polymers (CPs), such as polyaniline (PANI), polypyrrole (PPy), poly (3,4-ethylenedioxy thiophene) (PEDOT), polythiophene (PTh), and 2,2- polybithiophene (PBTh) and polyacetylene (PA). Usual methods for the preparation of polymer/CNT composites consist of the direct mixing of components in the melt or in solution, in situ polymerization of corresponding monomer solution in the presence of carbon nanotube; by chemical or electrochemical approaches, and by nanotube seeding approaches. The effectiveness of interfacial nanotube-polymer contact depends on the synthetic process. Direct mixing of carbon nanotube with polymer followed by sonication is straightforward; however the nanotube in such composites would easily get damaged, which consequently limits the applications of the resulting composite. In situ polymerization leads to the most effective interfacial contact compared to the direct mixing and the nanotube seeding approach, which has been reported as an efficient way to form conducting polymer. A number of reports have appeared highlighting the synergetic performance of PANI–CNT composites in certain applications including fuel cells, supercapacitors, and sensors.**[9]** The conducting polymer has received much attention because of their wide applications range. Among the several conducting polymer, Polyaniline (PANI) has been studied extensively due to its high electrical conductivity, abundant raw materials, easy synthesis, good environmental stability, cost effectiveness and simple redox chemistry**[10]**. The PANI-CNT nanocomposite is one of the versatile nanocomposite due to the numerous applications such as Gas sensor**[11-12]** Biosensor **[13],** Supercapacitor**[14],** Solar cell **[15],**Fuel cell]**[16],** corrosion protection **[17],** etc. Out of several synthesis methods of PANI-CNT nanocomposite reported literature, in-situ polymerization is the most use synthesis method as it enables grafting of polymer molecules on CNT, which leads to better dispersion coefficient and better interaction between CNT and polymer matrix. Incorporating CNT of various concentrations into PANI enhance the conductivity of PANI nanocomposite as CNT could have much higher electrical conductivity than PANI. The CNT could behave as conducting bridge between conducting domains of PANI thus enhanced the electrical conductivity of PANI **[18]**.

In the present work, we report the synthesis of PANI-CNT nanocomposite by in-situ polymerization. This work was aimed to obtain good dispersion of CNTs within PANI matrix to achieve enhancement in electrical properties of the nanocomposite.

A. Materials & Methods

Multiwalled carbon nanotube (99%) having outer diameter of 20-40nm and length of 1-2µm was obtained from Nanostructured and Amorphous Inc, USA. Aniline (99.9%), ethanol (99.9%), ammonium peroxydisulfate (98%) and hydrochloric acid were obtained from S.D. Fine Chem Ltd. All chemicals were of analytical grade. Aniline was double distilled before use. Solutions were prepared in deionised water.

B. Synthesis of PANI/CNT composite

The Polyaniline/MWCNT composite were synthesized by in-situ chemical oxidative polymerization by measuring different quantities of MWCNT (1% and 3% wt) dispersed in a solution of 1M HCl with ultrasonication for 2 hrs. To this solution aniline (0.05M) was added and the mixture was again ultrasonicated for 2 hrs for complete dispersion of the monomer and the CNT bundles. A freshly prepared precooked 1M solution of oxidant (Ammonium peroxodisulfate) was added drop wise (~20ml) to the mixture of monomer and CNT for 30 minutes with continuous stirring. The reaction was left for polymerization for 6 hrs. The PANI/MWCNT composite was obtained by filtering and rinsed several times with distilled water, ethanol respectively. The obtained composite was dried under vacuum at 60º C for 12 hrs.

C. Preparation of the pellets

The test samples of the PANI and its composites to be used were prepared in a pellet form with a diameter of 9 mm and an average thickness of 1 mm by applying a pressure of 5 ton using Pye-Unicam dye.

II. CHARACTERIZATION TECHNIQUES

The prepared pure PANI and its MWCNT-doped composites were structurally characterized via X-ray diffraction (XRD) using Philips powder X-ray diffractometer (Model: PW1710) in the 2θ range from 10◦ to 80◦. The Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer spectrum 100. FTIR spectrometer in the range of 400– 4000 cm−1 with the KBr pellets of the samples. Then the pure PANI and its MWCNT composites were morphologically analyzed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Their electrical conductivity was measured using the two-point probe technique with a Keithley multimeter and a Keithley electrometer.

III. RESULT AND DISCUSSION

The formation of tubular composites is believed to arise from the strong interaction between the aniline monomer and MWCNTs. The interaction possibly comes from the □□□ electron interaction between MWCNTs and the aniline monomer. Such a strong interaction ensures that the aniline monomer is adsorbed onto the surface of MWCNTs during the formation of tubular composites. MWCNTs, therefore, serve as the template and the core during the formation of tubular composites. Because of the random formation of MWCNT bundles, there are some special gaps between individual MWCNTs. Aniline molecules are wedged into such special gaps because of the strong interaction between the MWCNTs and aniline monomer and then in situ polymerization. As the polymerization proceeds, the growing PANI macro- molecules break down the CNT bundles into individual CNTs, and thus MWNTs can be dispersed into PANI matrices uniformly and individually, because of the site-selective interaction between the Quinoid ring of the polymer and MWCNTs, PANI.

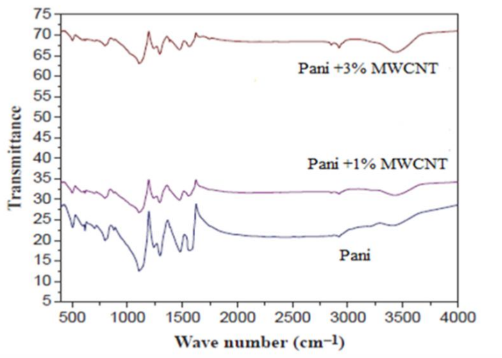

Fig. 1 FTIR spectra of pure PANI and PANI/MWCNT Composites

When CNTs are dispersed in an aniline/HCl solution, aniline hydro-chloride ions are adsorbed onto the nanotube surface. Upon the addition of the oxidant [(NH4)2S2O8],the adsorbed species are oxidized and form cation radicals, which initiate polymerization on the surface. The reaction takes place faster on the surface of CNTs than in the bulk because of the low activation energy (based on the principles of heterogeneous catalysis). This leads to the formation of the PANI shell over CNTs. Thus, the nanotubes act as a template for the formation of tubular composites. In a well-dispersed solution of CNTs, the adsorption of aniline hydrochloride will be high and uniform, and this can lead to the formation of a thicker uniform coating of PANI.

The FT-IR spectra of PANI & PANI/CNTs composites were shown in Figure 1.Spectrum of PANI shows peak at 3434cm^{-1} which is attributed to N-H stretching vibrations. The bands near 1600 cm^{-1} and 1453 cm^{-1}shows the Quinoid and benzenoidring vibrations respectively**[19]**. The absorption band at 1293.60 cm^{-1} is assigned to C-N stretching of secondary aromatic amines. The strong band at 1124cm^{-1} is a measure of degree of electron delocalization and hence it is characteristic peak of PANI conductivity. On incorporation of CNTs in PANI the peak at 1600cm^{-1}, 1453.45 cm^{-1} and 1125.63 cm^{-1} are shifted to 1588 cm^{-1}, 1463.45 cm^{-1} and 1116.74 cm^{-1} respectively. The red shift observed in the nanocomposites indicates the conversion of benzenoid structure to polaron structure in the PANI chains. Also there is an increase in the intensity of peaks. This shows effective degree of electron delocalization owing to the interaction between CNT and PANI **[1-2, 20]**.For the PANI/MWCNT nanocomposite no new absorption peaks found, the intensity of the nanocomposites decreased by increasing the amount of MWCNT such behaviour ensure the formation of PANI on the wall of MWCNTs by in situ chemical polymerization process. **[21].**

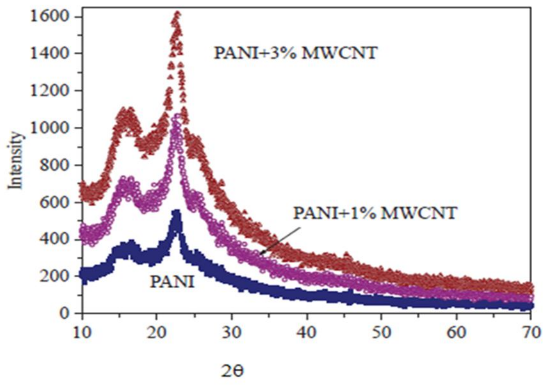

Figure 2: XRD pattern of PANI and PANI-CNT Composites

Figure 2 shows the XRD pattern of PANI, PANI MWCNT nanocomposite. The XRD pattern of pure PANI and PANI nanocomposite shows that the peaks are scattered at 2□ value between 20o and 30o, where the characteristic peak of PANI appeared at 20.5o and 25.55o corresponds to (020) and (200) crystal planes of PANI[22].Nanocomposite of PANI-CNTs show peaks similar to PANI and the peak intensity is also close to that of PANI. When CNT is incorporated into PANI matrix , the only peak characteristic of PANI is observed at 25.9^{o} . No additional crystalline peak is observed indicating that crystal structure of PANI is maintained in the nanocomposite. The formation of PANI MWCNT nanocomposite was due to π-π interaction between MWCNT and PANI [23-24]. This result confirmed the formation of nanocomposite and indicates that PANI and its nanocomposite have crystalline structure.

Figure 3 shows the SEM images of pure PANI, Pure MWCNT and PANI–MWCNT nanocomposites. The Pure PANI shows the formation of agglomerated and irregular granules of PANI. The average size of the granules is in the range of 100nm. PANI-MWCNT composites show the homogenous coating of PANI onto the CNT indicating that carbon nanotubes were dispersed in polymer matrix. Rough surface and increased diameter of the composites indicates the coating of PANI over CNTs since diameter of MWCNT was 30-40 nm. Nanocomposite shows new interwoven fibrous structure acts as conductive pathways and leads to high conductivity as compared to that of pure PANI.

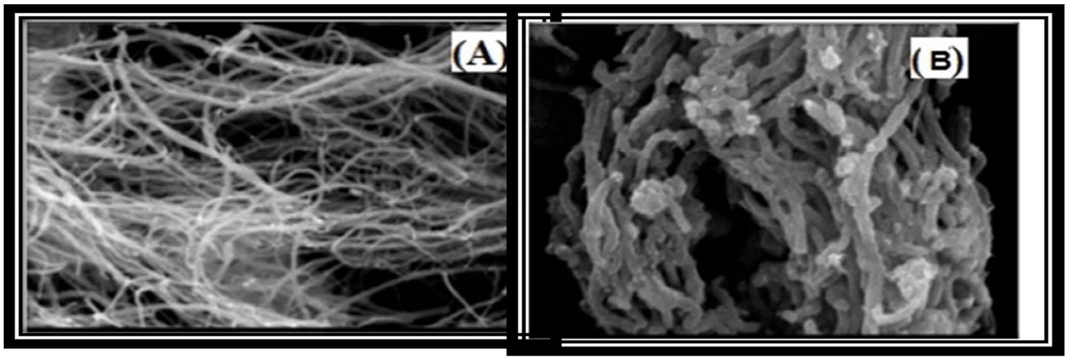

Figure 3 :Sem of (A) CNT and (B) PANI-CNT's nanocomposites

The thermal stability of PANI and PANI- MWCNT composites with different compositions has been analyzed using the Differential Scanning Calorimetric (DSC) curve, as shown in Figure 4.

The curve provides information on the energy variation during the processes that take place while the sample is being heated. From the DSC curve, it was observed that the glass transition value of the temperature for the composites increased with the addition of the MWCNTs. This indicates that PANI-MWCNT composites are more stable than pure PANI.

A. Temperature Dependence Of The Dc Electrical Conductivity

Variation of electrical conductivity of Pani-MWCNT composites with temperature is shown in figure 5.The electrical conductivity was calculated within a temperature range. It was found that the DC conductivity, for all the samples, increased with the increase in temperature. Such enhancement in conductivity can be attributed to the interaction between the Quinoid rings of the PANI and the MWCNTs **[25].**

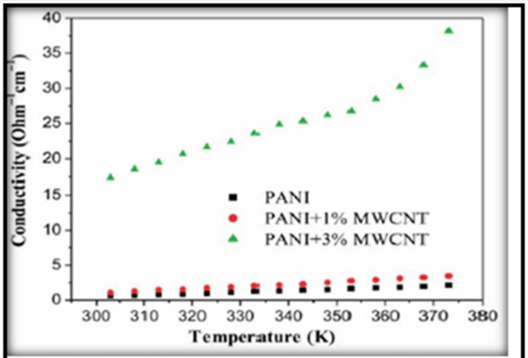

Figure 5. Variation of the conductivity as a function of the temperature for the PANI and the PANI/MWCNT composites.

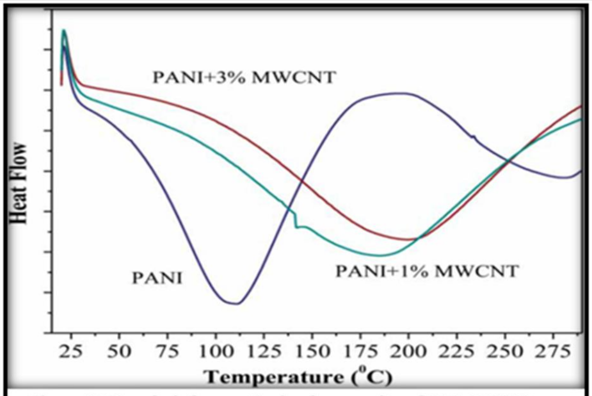

Figure.4 DSC analysis for pure Pani and composites of PANI- MWCNT

From the analysis,it was found that MWCNTs serve as conducting bridges for pure PANI **[26]**. This improvement in the DC electrical conductivity of PANI/MWCNT composites comes from the effective dispersion of MWCNTs onto a PANI matrix (as shown in the SEM images), which enhances the electronic transport properties. In summary, it was observed that the DC electrical conductivity of PANI is enhanced with an increase in the temperature and concentration of the MWCNTs.

IV. CONCLUSION

PANI-MWCNT nanocomposite was successfully synthesized by chemical oxidative polymerization by using monomer Aniline. FTIR, XRD and SEM show the effective structural modification confirm the coating of PANI layer on the MWCNT surface. The measurement of DC electrical conductivity of doped samples showed that MWCNTs serve as conducting bridges for pure PANI. Thus, the present study suggests that PANI/MWCNT composites are better electronic materials than pure PANI, and that increasing the concentration of MWCNTs in PANI can change the behaviour of PANI from that of a semiconductor to a metal. Another important effect of MWCNT doping is the increase in the thermal stability of the PANI

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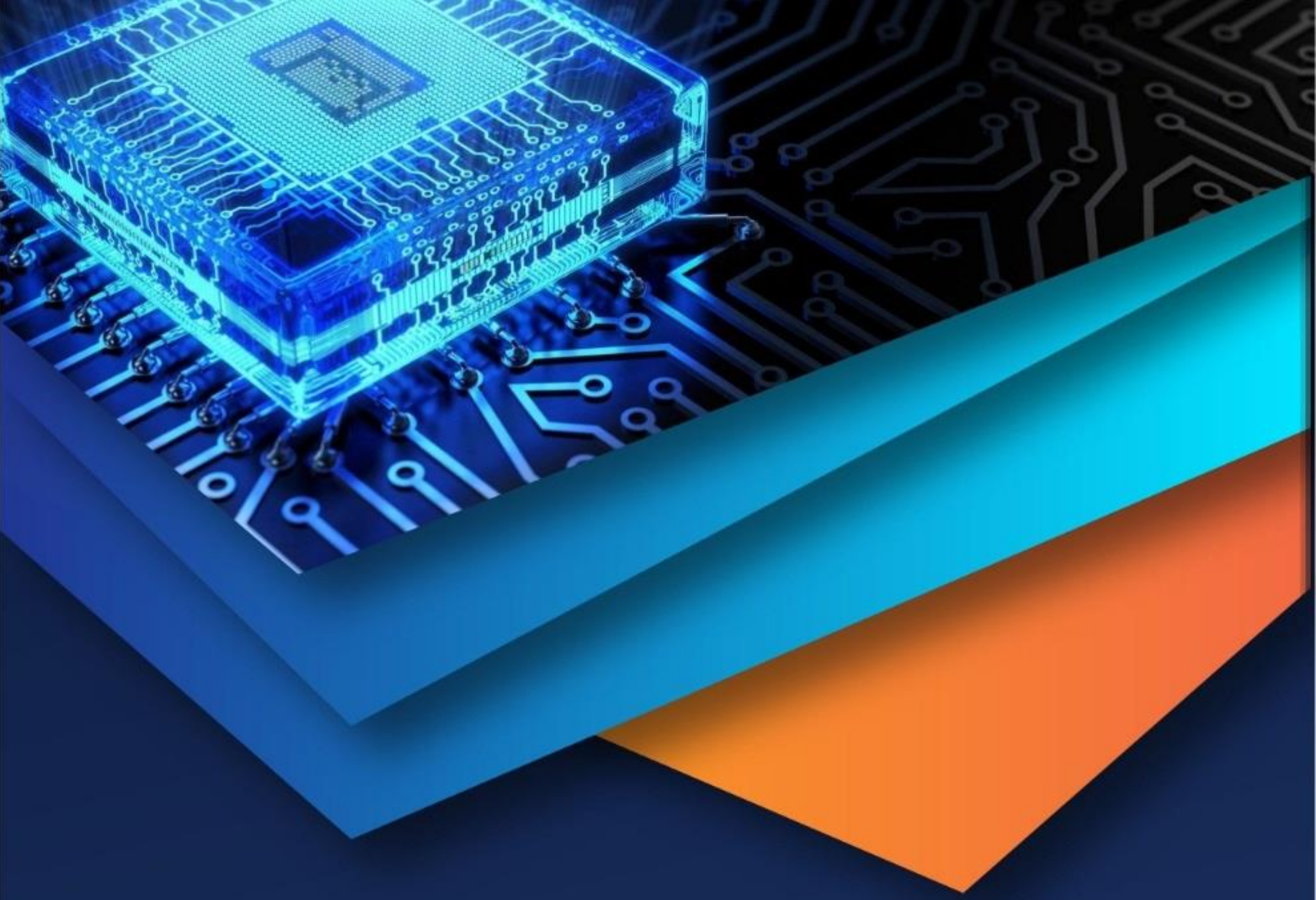

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