



Synthesis and Characterization of Polypyrrole/Carbon Nanotubes Composites

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Composites of polypyrrole with multi-walled carbon nanotubes prepared by CVD method were synthesized by chemical oxidation method using hexahydrated ferric chloride as an oxidant in aqueous solution. The synthesized composites were characterized for their structural, thermal and DC conductivity analysis with fourier transform infrared spectroscopy, scanning electron microscopy, thermal gravimetric analysis, differential scanning calorimeter and four-probe method respectively. The percolation threshold for DC conductivity and thermal stability was 2 % of carbon nanotubes contents in polypyrrole matrix due to better conjugation, homogeneous dispersion and compactness indicated by FT-IR and SEM studies. Combination of polypyrrole and carbon nanotubes also present enhanced thermal properties with the increase of weight percentage of carbon nanotubes in composites.

Key Words: Carbon nanotubes, Composites, DC conductivity, SEM, Differential scanning calorimeter.

INTRODUCTION

In recent times one-dimensional nanostructures, such as carbon nanotubes and conjugated polymers have become the subject of passionate investigations due to their conducting properties promising in the synthesis of materials having unique optical and electronic properties and can be used in field effect transistors, nanoelectronic devices and probe tips for scanning probe microscopy¹⁻³. Among numerous kinds of conducting polymers, polypyrrole (PPy) is one of the most attractive organic semiconducting polymer with remarkable features of their potential applications, relatively high conductivity, remarkable environmental stability and facile synthesis^{4,5}. Electrical conductivity of conjugated polymers can be tuned over a wide range from insulating to metallic by proper doping with appropriate dopants. But the conjugated polymers are insoluble, infusible and non-processable due to their strong intermolecular interactions. Composite formation is an attractive route to overcome the drawbacks of conducting polymer to improve their mechanical properties^{6,7}.

In this work multi-walled carbon nanotubes were used to prepare polypyrrole-carbon nanotubes composites to study the behaviour of these composites by various spectroscopic techniques. In previous works, we have characterized the electrical, structural and thermal properties of conjugated polymer composites of polypyrrole with α -ferric oxide and zinc oxide, respectively^{8,9}. In this paper, we focus on electrical, structural and thermal characteristics of polypyrrole/carbon nanotubes

composites with different particle loadings ranging from 1 to 4 % of polypyrrole contents. So a four-probe electrical measurement is necessary to reveal the intrinsic electronic transport properties of polymer. Conductivity is measured as a function of doping level, conjugation chain length and compactness.

EXPERIMENTAL

Pyrrole (C_4H_5N) monomer from fluka was distilled under reduced pressure prior to use and stored in dark at 0 °C. iron(III) chloride hexahydrated ($FeCl_3 \cdot 6H_2O$) (analytical grade) from Merck was used as a radical oxidant in the aqueous medium. Multiwalled-carbon nanotubes were prepared by CVD method and were used after purification. All solutions were prepared in double distilled water.

Synthesis of polypyrrole and polypyrrole-carbon nanotubes composites: Polymerization of pyrrole monomer was carried out in situ chemical oxidative environment⁸. During the polymerization of polypyrrole different wt. % of carbon nanotubes (1-4 % of polypyrrole yield) were added to the reaction mixture and stirred for 3 h at constant temperature of 8 °C under nitrogen atmosphere and resulting composites were named as CPNT-1, CPNT-2 and CPNT-4 respectively.

FT-IR analysis: Structural analysis of polypyrrole, carbon nanotubes and their composites were investigated by using a Perkin Elmer RXI FT-IR over the wavenumber range of 4000-650 cm^{-1} . All samples were characterizes as KBr discs¹⁰.

SEM analysis: Phase analysis of polypyrrole, carbon nanotubes and their composites were investigated by a scanning electron microscope followed by back scattered electron image mode. Hitachi-3400 N scanning electron microscope operated at accelerating voltages of 15 KV and 20 KV were used for microstructure analysis of polypyrrole and polypyrrole-carbon nanotubes composites.

Thermal gravimetric analysis: The thermal stability of pure polypyrrole and polypyrrole-carbon nanotubes composites were examined by SDT Q600. The samples were heated from 25 to 800 °C under an air atmosphere flow condition with a flow rate of 20 °C/min. An aluminum pan was used as a reference. The calorimeter cell was flushed with 100 mL min⁻¹ of nitrogen.

Differential scanning calorimeter analysis: The glass-transition temperature are investigated by DSC analysis, performed by SDT Q600 differential scanning calorimeter with a heating rate of 10 °C/min and a nitrogen flow rate of 100 mL/min. The samples are sealed in a standard aluminum pan. The runs were performed from 25-800 °C.

DC electrical conductivity: Standard four probe method was used to measure the DC electrical conductivity at room temperature (25 °C). Powdered samples of polypyrrole and its composites were pressed in the form of disk pellets with a diameter of 25 mm by applying a pressure of 80 MPa in a hydraulic press and the average thickness was *ca.* 1 mm. Voltage applied across circuit was measured by AVO meter (M 2007) and corresponding current was measured from professional Pro's kit multimeter. Conductivity (S. cm⁻¹) was measured as reported previously^{8,9}.

RESULTS AND DISCUSSION

Fourier transform infrared analysis: Fig. 1 represents the FT-IR spectra of pure polypyrrole, carbon nanotubes and the polypyrrole-carbon nanotubes (2 wt. %) composite. The band at 1539, 1223, 1028 and 700 cm⁻¹ are typical signals of polypyrrole¹¹⁻¹⁶. The FT-IR spectra of the polypyrrole-carbon nanotubes composites are almost identical to that of polypyrrole, however, the peak shifted at 1520 cm⁻¹ (C=C stretching vibration), 1217 cm⁻¹ (breathing vibration), 1042 cm⁻¹ (C-H in-plane deformation) and 673 cm⁻¹ (C-H out-of-plane bending) for CPNT-2 due to absorption peaks of carbon nanotubes at 1250 and 1545 cm⁻¹ due to C=C vibrations. The shifting of peaks towards higher frequencies and the increase in intensity of the characteristics peaks of polypyrrole in composites indicate strong interactions between polymer backbone and carbon nanotubes¹⁷.

Scanning electron microscopy analysis: Fig. 2 shows the SEM micrographs of polypyrrole-carbon nanotubes composites (1-4 wt % of polypyrrole). A high magnification of 2K reveals the growth of carbon nanotubes along the polypyrrole chains in a granular pattern. Hence, a network of carbon nanotubes and granular polypyrrole has been formed in case of composites. In addition to grey scaled particles some white particles are also seen in the micrograph, these are due to the electron beam charging effect. It is also seen in the micrographs that addition of carbon nanotubes produces compactness with the decrease of grain boundary volume from 9-2 μm with the increase in wt. % of carbon nanotubes due to

high surface area of carbon nanotubes¹⁸. While the cluster and granular structure of polypyrrole is maintained even after the addition of carbon nanotubes in composites.

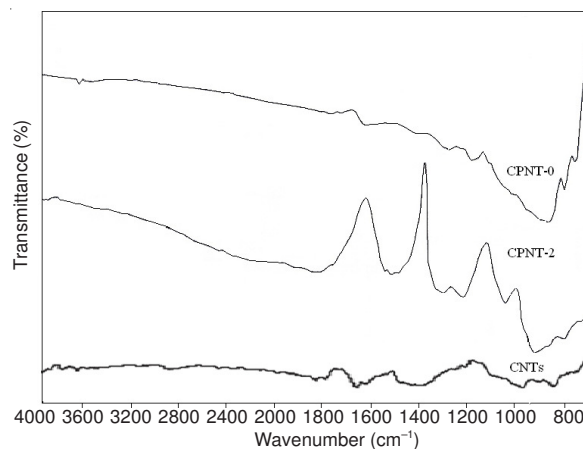


Fig. 1. FT-IR spectra of polypyrrole/carbon nanotubes composites

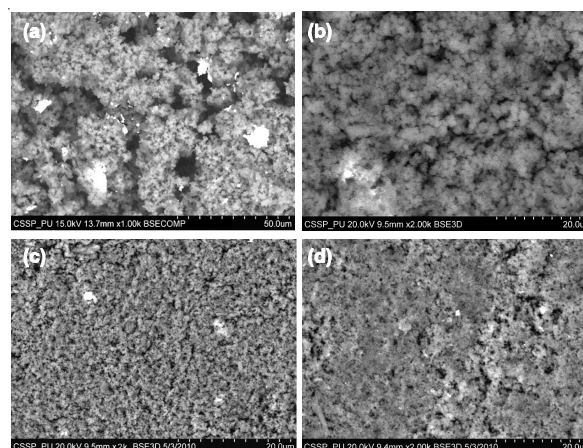


Fig. 2. SEM micrographs of (a) CPNTs-0 (b) CPNTs-1 (c) CPNTs-2 (d) CPNTs-4

DC conductivity measurements: The relation between DC conductivity and carbon nanotubes content in polypyrrole matrix was presented in Fig. 3a. The percolation threshold for conductivity in case of polypyrrole-carbon nanotubes composites was 2 % of carbon nanotubes in polypyrrole matrix. The conductivity of pure polypyrrole is 6.00 S. cm⁻¹ and increases from 11.88-16.20 S. cm⁻¹ when the wt. % of carbon nanotubes in polypyrrole increases from 1-2 % of polypyrrole contents and then dramatically decreases to 13.95 S. cm⁻¹ for CPNT-4. The increase in DC conductivity may be due to the strong physiochemical interactions between polypyrrole and carbon nanotubes, compactness, reduction in grain size and highly extended chain conformation of polypyrrole and decrease in conductivity may be due to the loose of grain boundaries and decrease in the intensity of absorption peaks to confirmed the less delocalization of electrons over the polymer chains inferred from SEM and FT-IR analysis respectively.

Thermal gravimetric analysis: Thermal gravimetric analysis of pure polypyrrole and polypyrrole-carbon nanotubes composites with different particle loading (1-4 wt. % of polypyrrole) are done in the temperature range of 25-800 °C (Fig. 3b). The initial weight loss of 10.60 % is observed at

temperature 110 °C, which is attributed to the expulsion of moisture from the polymer. The weight loss was found to be 19.30 % at 250 °C due to degradation of polymer chain. The decomposition step initiate from 250 °C resulting in weight loss of 64.37 % up to 600 °C due to release of C, H and N moieties of polypyrrole unit¹⁹. The weight left at 800 °C is 52.44 % due to carbon residue. The composites remain stable up to 800 °C with a weight loss of only 44, 39 and 35 % for CPNT-1, CPNT-2 and CPNT-4 respectively. It is observed here that the composites of polypyrrole-carbon nanotubes are thermally more stable than pure polypyrrole and it may be attributed towards the higher thermal stability of carbon nanotubes up to 3255 °C²⁰. Thermal stability was found to be increased linearly with the increase in wt. % of carbon nanotubes in polypyrrole matrix (Table-1).

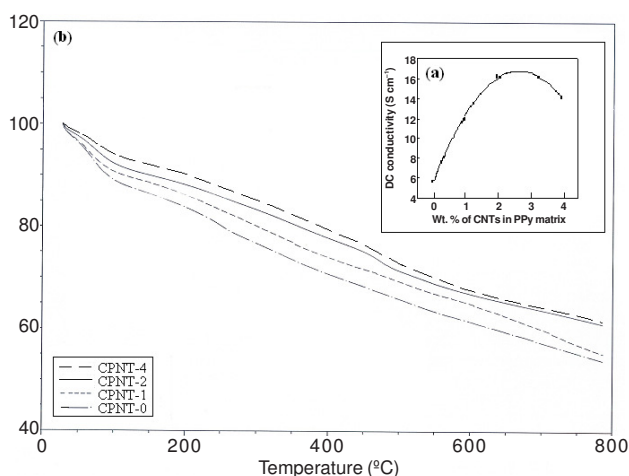


Fig. 3. Conductivity versus carbon nanotubes contents in polypyrrole-carbon nanotubes composites; (b) Thermal gravimetric analysis curves of polypyrrole-carbon nanotubes composites

Differential scanning calorimeter analysis: Polypyrrole has a broad endothermic plunge at 74 °C, which is the glass transition (T_g) of polypyrrole as shown in Fig. 4. In case of its composites T_g increases to 77.77 °C with no other endothermic plunge to predict their low crystallinity (Table-1). The addition of carbon nanotubes affects the T_g of polypyrrole due to better conjugation and strong physicochemical interactions between polypyrrole and carbon nanotubes as inferred from FT-IR and SEM analysis.

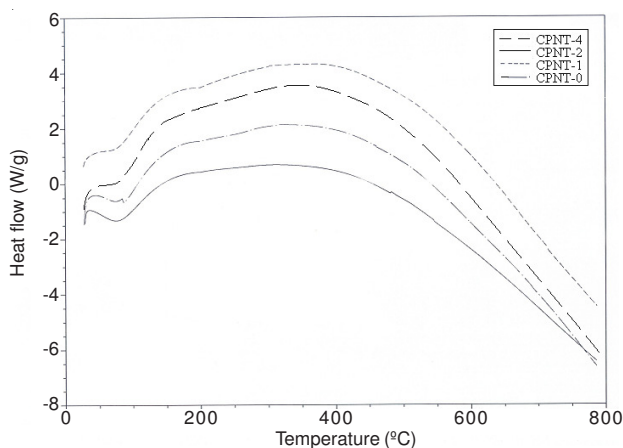


Fig. 4. DSC curves of polypyrrole-carbon nanotubes composites

TABLE-1
TGA AND DSC DATA OF PPY-CNTs COMPOSITES

Temperature (°C)	Weight lose (%)			
	CPNT-0	CPNT-1	CPNT-2	CPNT-4
110	10.60	9.9	8.39	8.32
250	19.30	17	14.19	13.27
515	32.25	31.22	29.38	28.26
600	35.63	34.96	33.14	31.59
800	47.56	44.21	38.98	35.02
T_g °C	74	77.77	77.77	77.77

Conclusion

Composites of polypyrrole-carbon nanotubes were prepared by facile chemical oxidation method and were characterized for their structural, thermal and electrical properties. The percolation threshold for conductivity is 2% of carbon nanotubes in polypyrrole composites. FT-IR analysis shows an interaction between polypyrrole and carbon nanotubes to change their conformation by the shifts of absorption bands to lower frequencies and increased in the intensity of peaks to confirm the more delocalization of electrons to enhance conductivity as compared to pure polypyrrole. SEM results show the complete encapsulation of carbon nanotubes in polypyrrole matrix with the reduction of grain size. Thermogravimetric analysis showed that incorporation of carbon nanotubes has increased the thermal stability of polypyrrole.

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