Electrical conductivity and dielectric behavior of multiwalled carbon nanotube incorporated polypyrrole nanocomposites.

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Abstract:

Polypyrrole (PPy) / multiwalled carbon nanotube (MWCNT) composites have been synthesized by in-situ chemical oxidation polymerization and the samples were characterized by Fourier transform infrared spectroscopy, X-ray diffraction analysis and scanning electron microscopy to understand the structure and morphology. The frequency dependent conductivity and dielectric constant of the nanocomposites were investigated in the low frequency range from 10 Hz to 1 MHz. The variation of AC conductivity with frequency obeyed the power law and studies on dielectric property showed coupled relaxation contribution. The conductivity of the composites was found to depend on the MWCNT content. Also, the dielectric constant and dielectric loss in these composites showed dependency on MWCNT content with percolation behavior. These conducting composites were further used as humidity sensors by observing change in resistance with relative humidity. The observed electrical and sensing properties suggest that these nanocomposites can be optimized for useful technological applications.

1. Introduction

During the previous couple of decades, conducting polymers and conducting polymer composites have been widely explored for technologically important applications in electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane and sensors [1, 2]. Conducting polymers exhibit tunable electrical property, diverse mechanical and optical properties with good environmental stability [4-6]. Specifically as battery electrode materials, conducting polymers provide better processibility into unusual shapes and sizes, lightweight, low cost, less corrosive nature and compatibility with organic liquid and solid electrolytes [1, 4]. Among conducting polymers, polypyrrole is one of the most extensively studied polymers because of its high environmental stability, high electrical conductivity, high thermal stability and can also be easily oxidized both chemically and electrochemically [7,8]. Polypyrrole has attractive applications like drug delivery, gas separation and various sensors [10, 11]. Polypyrrole is being investigated for new possible applications such as artificial muscle fibers to be used in devices to mimic as biological nano and micro actuators, in low temperature fuel cell technology to enhance the catalyst dispersion in the carbon support layers, to sensitize cathode electro catalysts, etc.[12].

Since the middle of the last century, composite materials research has contributed new types of materials with better properties by selecting appropriate fillers as their nature significantly affects the resulting composite. The present research focus multifunctional application of polypyrrole (PPy) / multi-walled carbon nanotubes (MWCNT) composites. As an effective nano-structured filler MWCNT have increasing electronic applications due to their extraordinary electrical, thermal and mechanical properties. In PPy/MWCNT composites, length, diameter, aggregation state and aspect ratio of MWCNT is expected to affect the various properties of the resulting material [13-16]. Recent high-tech applications, such as satellite TV, sensors, solar cells, electromagnetic shields, energy reservoirs, heating systems and electro – optical devices, make use of polymer-based composites possessing electro-conductive properties [6]. Energy storage devices like super capacitors, batteries and conversion devices like fuel cells, thermo electric devices, photovoltaic cells and LED's are important requirements for improving our energy preservation and to overcome energy crisis in the present era[18]. Humidity sensing and controlling is of significant relevance in various fields such as food processing, agriculture, medical, aviation systems and electronic device manufacturing units, etc.[20-22]. To achieve the desired application potential of the PPy/MWCNT composite, here we report the electrical characteristics and humidity sensing response of these composites synthesized via in-situ oxidative polymerization technique.

2. Experimental

2.1 Materials

Pure pyrrole analytical grade purchased from Hi-media chemicals, $Fecl_3$ and ammonium persulphate analytical grade from Sd fine chemicals, Green tea leafs from Apollo Pharmaceuticals and MWCNT from Ad Nano chemicals.

2.2 Preparation of PPy/ MWCNT composites

Iron decorated polypyrrole was prepared by using green tea extract (Reducing agent) &1.54mole $Fecl_3$. Green tea extract prepared by using 5grams of green tea leafs with 200ml distilled water boiled till to reduce to 100ml. This extract was cooled to room temperature. Then 1.54 $Fecl_3$ was added kept at room temperature about 24 hours. Fe^{3+} ions reduced to iron nanoparticles. In-situ chemical polymerization method was employed to incorporate iron nanoparticles into the polypyrrole matrix with ammonium persulphate act as an oxidizing agent. Similarly polymerization is continued with the chosen weight percentage (wt.%) of MWCNT to synthesize PPy/ MWCNT composites PM 1(PPy with 5wt.% MWCNT), PM 2(PPy with 10wt.% MWCNT), PM 3(PPy with 15wt.% MWCNT) and PM 4 (PPy with 20wt.% MWCNT).

3. Results and discussion

3.1 Structural and morphological characterization

3.1.1 XRD results

The structure of the composites samples was investigated by X-ray diffraction (XRD) measurements. The XRD patterns of pure PPy and PPy/ MWCNT composites are shown in Fig.1 Pure PPy(Fig.1a) exhibited a broad amorphous diffraction peak at $2\grave{e} = 18^0$-32^0 range is consistent with the standard XRD pattern of PPy. [13] These peaks can be attributed to the scattering from bare polymer chain at the inter-planar spacing. The XRD patterns of the composites indicates the modified structure of PPy in the presence of MWCNT.

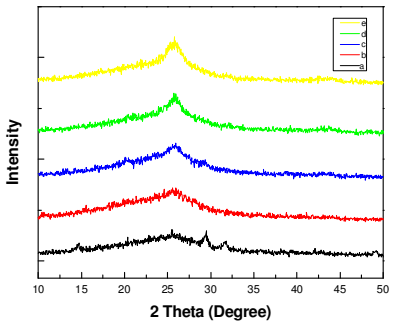


Fig.1. XRD patterns of (a) pure PPy, PPy/MWCNT composites at (b) 5wt.%, (c) 10wt.%, (d) 15wt.% and (e) 20wt.% MWCNT content

3.1.2 FTIR spectra analysis

FTIR spectroscopy is a useful technique in characterizing structure of materials, by analyzing the micro-transformations in FTIR spectra. FTIR spectra of PPy/ MWCNT composites showed changes of peak position and intensity. This reveal that PPy/MWCNT composite is not a simple mixture of two phases, PPy matrix and MWCNT filler but a composite with MWCNT incorporated in PPy.

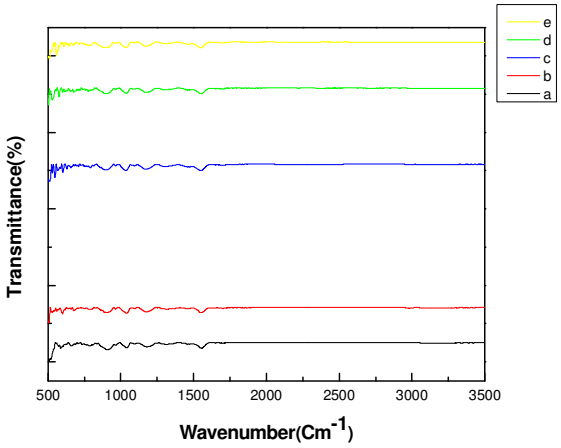
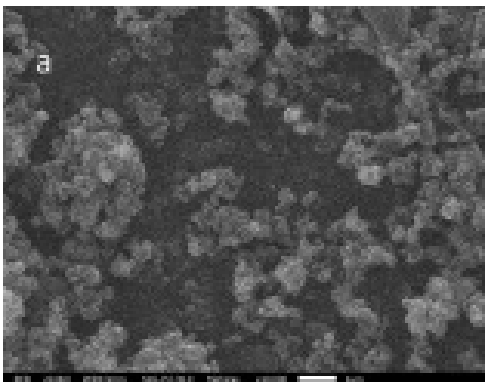
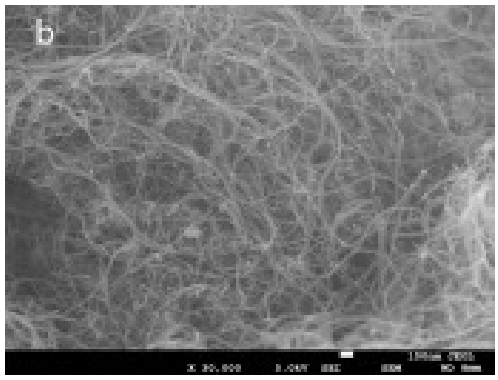


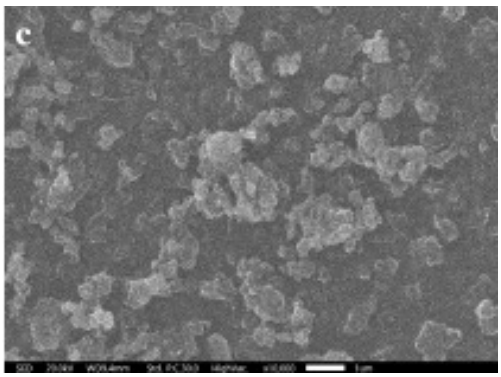
Fig.2. FT-IR Spectrum of (a) pure PPy, PPy/ MWCNT composites at (b)5wt.%, (c)10wt.%, (d)15wt.% and (e)20wt.%

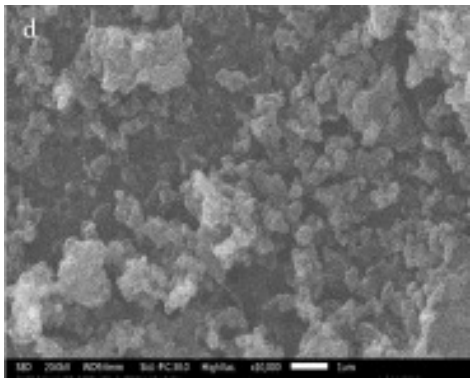
3.1.3 SEM studies

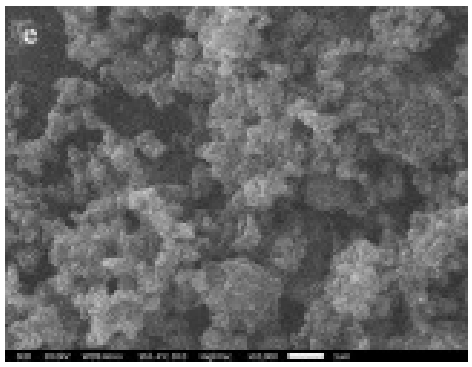
Fig. 3 shows the SEM image of PPy, MWCNT and PPy / MWCNT composites. SEM image of the composites indicates that MWCNT is incorporated into PPy matrix as confirmed by FTIR spectra [13]. The formation of PPy / MWCNT interface is expected to improve the transport property and sensing response of the sample.











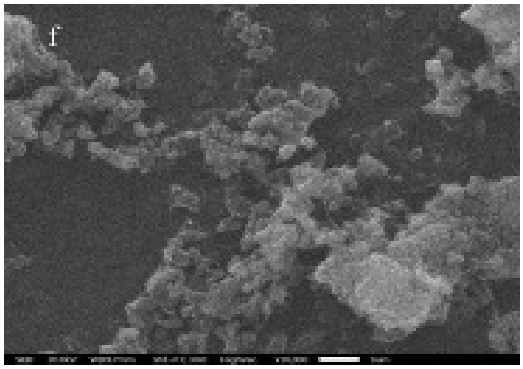


Fig.3 – SEM image of (a) pure PPy, (b)MWCNT, PPy/MWCNT composites at (c) 5wt.%,(d)10wt.%, (e)15wt.%, (f)20wt.% MWCNT content

3.2Transport property analysis

3.2.1 DC conductivity

The temperature dependent DC conductivity (ódc) characteristics of PPy/MWCNT composites are presented in Fig.4. The increase of DC conductivity of the composites was minimal in the low temperature region up to 353 K and increased thereafter steadily up to 473 K. That is, conductivity of all the composite samples (in the range $1.4x10^{-2}$ S cm-1 to 0.3 S cm-1) increased with increasing temperature exhibiting typical semiconducting behavior.

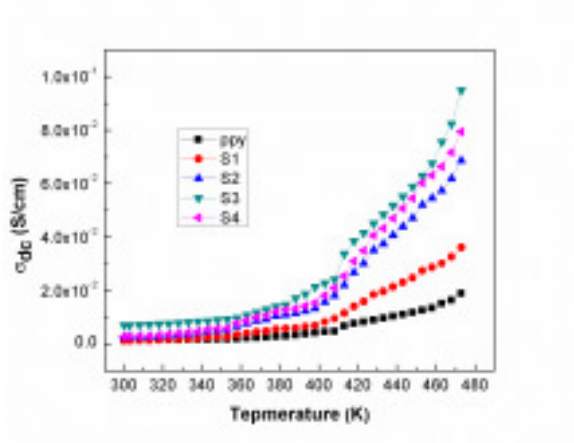


Fig.4 Temperature dependent DC conductivity ($ó_{dc}$) of PPy/MWCNT composites

3.2.2 Low frequency AC conductivity

Low frequency AC conductivity of PPy/MWCNT composites are represented in Fig.5.The frequency dependent conductivity of the composites in the range of 10^{-2} to 10^{-1} is attributed to the semi crystalline nature of the PPy/MWCNT composites. The AC response of all the composites exhibited a frequency independent conductivity in the low frequency region up to 2 kHz and then increased as the frequency increased. This frequency independent plateau followed by a high frequency dispersed region in these composites obeyed the power law indicating the universal behavior of the ac conductivity in disordered media [24].

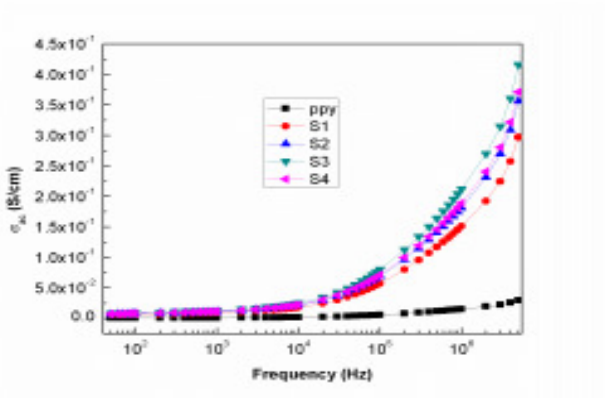


Fig. 5 Temperature dependent AC conductivity ($ó_{dc}$) of PPy/MWCNT composites

3.3 Humidity sensing properties

Fig.6 shows the variation of resistance for PPy/MWCNT composites with relative humidity (RH). The change in the resistance of the composites with various relative humidity levels was monitored. From the plots we observe the decrease in resistance of the composite with increase in the level of relative humidity (%RH). The change in resistance is quite significant as the content of MWCNT in PPy increases. The decrease in resistance with increase in relative humidity is due to the adsorption of water molecules by the surface of the samples. The morphological features of PPy/MWCNT composites enhance the charge transfer across the polymer chains giving better sensing response [25]. A maximum sensitivity was obtained for 15 wt.% loading of MWCNT in PPy matrix.

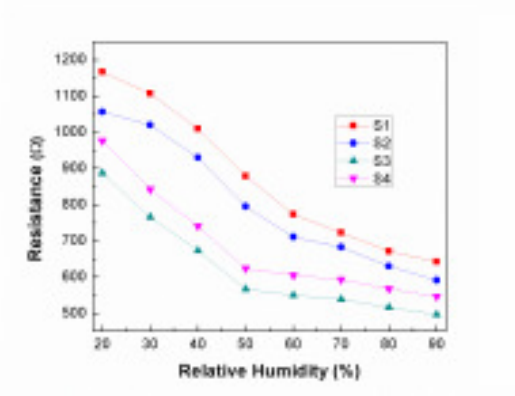


Fig. 6 Variation of resistance versus % of RH of PPy/MWCNT composites.

4. CONCLUSION

The observed electrical properties of the PPy/ MWCNT composites display the prospects of various technological applications of these composites. The variations in the DC conductivity, AC conductivity, and humidity sensing response of the composite with varying MWCNT concentration is attributed to the conformational changes in PPy matrix.

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