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Exploration of thermal stability studies of MWCNT-conducting polymer based composites for heat sensing application

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Abstract
Composites of multiwall carbon nanotubes (MWNTs), electrically conducting polymers like Polyaniline (PANI), and poly (3, 4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT: PSS) were prepared by following solution casting method. MWCNTs were functionalized with oxidative acid (5M HNO_3) treatment schemes to improve the adhesion between the polymer and carbon nanotubes by a II-II stacking interaction. Structural and morphological characterization of composites has been carried out by means of Field emission scanning electron microscope (FESEM) and High resolution transmission electron microscope (HRTEM). A detailed temperature dependent resistance study of both the composites was performed to examine the thermal properties of both the composites. MWCNT-PEDOT: PSS composite was found to show improved thermal stability than MWCNT-PANI composite hence was expected as the better candidate for heat sensor applications. MWCNT-PEDOT: PSS composite was further evaluated for its heat sensing response and was found to show excellent response, less response and recovery time and good reproducibility up to 190 ºC where the polymer film without MWCNTs was found to show the same results up to 100 ºC only.

Keywords: Carbon nanotubes, conducting polymer composite, thermal treatment, heat sensor

Introductions

Carbon nanotubes (CNTs) have attracted the attention and interest of researchers in many fields because of their remarkable properties leading to technological applications in different fields. Nanocomposite is one such application where nanoscale features, nano-particles, or nanofibers are introduced in the structure to obtain excellent mechanical, thermal, electrical, and functional properties.

Incorporation of CNTs into various matrix materials such as polymer ceramic and metal oxide, has been employed these days since it offers further scope for improvement in its properties for selective applications. CNT-polymer matrix composite is the most widely investigated, primarily due to the relative ease of preparation techniques compared to other two. Organic conducting polymers have received increasing attention as possible transparent and conductive materials because of their efficacious optical and electronic properties, and potential applications in flexible electronic devices. Reinforcement of CNTs in conducting polymer (CP) matrix represents a new class of material as some conducting polymers can behave like semiconductors due to their heterocyclic compounds which display physicochemical characteristics.

However, the implementation of CNTs into usable devices has historically been limited. The primary limitation has been due to the typical aggregation of as-grown CNTs into bundles through strong van der Waals bonding. From practical device applications point of view, these bundles must be broken. The other alternative is to make individual (one) nanotube-based sensor devices that have been previously demonstrated to circumvent these challenges but with little success in terms of its ability to produce large amounts of identical and pure tubes of the same size and structure.

Unmodified CNTs are very hydrophobic yet are also difficult to disperse in non-polar organic solvents, and some organic solvents such as DMF (dimethylformamide) have actually been shown to damage the CNT structure. Various methods have been used by researchers to disperse CNTs into solution including oxidative acid treatment and use of surfactants. Hence the application of CNTs-conducting polymers in flexible electronic devices is a serious concern to researchers globally the main objective of this paper is to to successfully fabricate thermally stable MWCNT-conducting polymer composite with improved the adhesion between the polymer and carbon nanotubes and to utilize it for heat sensing applications. In this work, two types of polymers composites (MWCNT with PEDOT: PSS and PANI) were prepared and their thermal stability study was carried out. MWCNT-PEDOT: PSS composite was found to show better thermal stability than MWCNT-PANI composite and when tested for heat sensor application, PEDOT: PSS composite was found to exhibit excellent response, small response and recovery time, good repeatability and complete recovery then PEDOT:PSS polymer.

Experimental

Purification and Functionalization of MWCNTs

MWCNT with outer diameter 20-30 nm and length of 6-15 µm were used in this work. They were first purified by heating at 400°C for 5 h in air to remove carbonaceous impurities and then ultrasonicated for 1 h using Ultrasonicator (model Elmasonic P) at 37 kHz frequency (50Watt), in 5M HNO3. MWCNT-acid solution was refluxed at 70°C for 5 h with constant magnetic stirring followed by filtration of the acid mixture using Nylon Membrane filter paper with pore size of the order 0.2 µm. The residue was re-suspended in deionized water obtained from a Millipore system. This process was repeated several times until the pH of the solution reached up to neutral value. CNTs were functionalized with oxidative acid (5M HNO_3) treatment schemes to improve the adhesion between the polymer and carbon nanotubes by a II-II stacking interaction.

Preparation of MWCNT Conducting Polymer Composites

MWCNT composites with PEDOT: PSS and PANI were fabricated by solution casting method. Former was synthesized by mechanical mixing MWCNT in 5 mL of PEDOT: PSS polymer solution while later, by mixing MWCNT in Polyaniline solution (100 mg polyaniline salt in 50 mL propanol). Then both the prepared solutions were rigorously stirred for 24 h at room temperature (RT). These composites were obtained in solution form and casted on alumina substrate, and dried for 1 h at 100°C. On the other hand, two reference samples were prepared on different substrates by coating polymer (PEDOT: PSS and PANI) exclusively using spin coating.

Material Characterization

To study the effect of acid treatment, FTIR spectra of MWCNTs (before and after acid treatment) were recorded and compared (using Bruker, Vertex 70 V). Field emission scanning electron microscope (FESEM) (FEI, Nova NanoSEM 450) and High resolution transmission electron microscope (HRTEM) (FEI, TECNAI300) images were recorded to examine the surface morphology of MWCNTs polymer composite films. All the gas sensing measurements (electrical measurements) were recorded at room temperature using electrical characterization unit (Keithley 4200- SCS).

Results and Discussions

Characterization

FTIR Analysis

Figure 1 (a) and (b) shows the FTIR spectra of MWCNTs before and after acid treatment. Absorption peaks at 3430, 1710, 1641, 1556 and 1200 cm^{-1} can clearly be observed in Figure 1(b) while these peaks are absent in FTIR spectrum ofuntreated MWCNTs as shown in Figure 1 (a). The peak at ~1710 cm-1 is clearly assigned to the C=O stretching vibration in acid treated MWCNTs and developed due the production of carboxylic acid groups. The two peaks around 1556 and ~1200 cm^{-1} are attributed to the graphitic structure of carbon nanotubes. The new peak assigned to the stretching mode of quinone group was located at 1641 cm^{-1}.The broad peak at ~3430 cm^{-1} is assigned to the O-H stretching vibration.

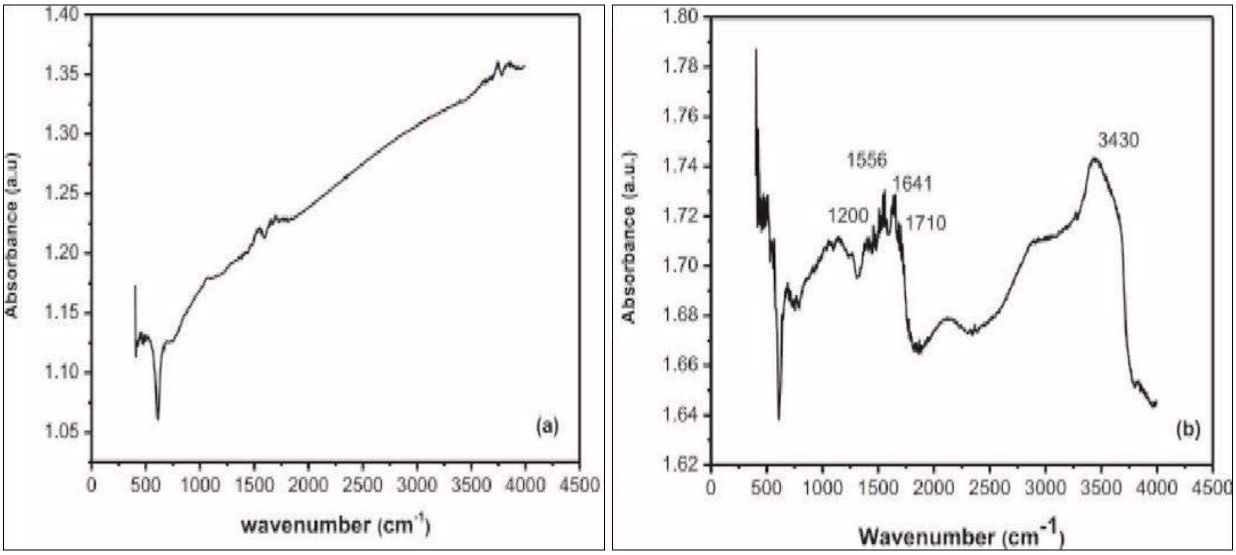

Fig 1: FTIR spectra of MWCNTs (a) before and (b) after acid treatment

These observations are direct evidence for introduction of a carboxylic acid group on the nanotubes. This also indicates that treatment with HNO_3 acid could make carbon nanotubes surface rich in functional groups. In addition, some defects are also created due to acid treatment because of which MWCNTs surface activity increases, this in turn, is very favorable to enhance sensitivity of gas sensor.

FESEM and TEM Analysis

Figure 2 and 3 shows the FESEM and HRTEM images of both MWCNT- PEDOT: PSS and MWCNTPANI composite films respectively. The higher magnification FESEM and HRTEM images clearly show a uniform coating of PEDOT: PSS and PANI polymers on the outer wall of the MWCNTs. Hence we conclude that both polymers are successfully coated onto the outer surfaces of the MWCNT, resulting in well dispersed CNT-polymer matrix composite.

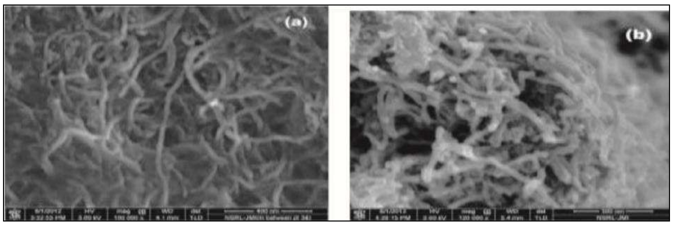

Fig 2: FESEM image of (a) MWCNT-PEDOT: PSS and (b) MWCNT-PANI Polymer Composite Pilm

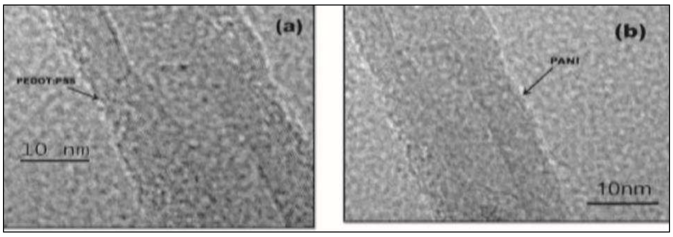

Fig 3: HRTEM Image of (a) MWCNT-PEDOT: PSS and (b) MWCNT-PANI polymer Composite Film 3.3. Thermal stability studies: A detailed analysis

The thermal properties of MWCNT-PEDOT: PSS and MWCNT-PANI composite films, in an air atmosphere, were investigated by performing a temperature dependent resistance study. To scrutinize the temperature dependent resistance characteristics, silver electrodes were made (using screen printing) at the two end terminals of prepared MWCNT-polymercomposite films and then annealed at 100°C in air. Samples were finally patterned on PCB (printed circuit board) for all electrical measurements. The annealed composite film was placed in a small and sealed chamber made up of steel with heater-cooler arrangement inside (Linkam, UK). In order to evaluate the effect of heating on the resistance of MWN Tpolymer composite film, heating procedure, controlled by a temperature controller and subsequent cooling to room temperature was followed as shown in Figure 4 MWCNT-PEDOT: PSS composite film was heated to 190ºC for a fixed duration in a step sequence with step of 20 °C as shown in Figure 4 (a), where as MWCNT-PANI composite film was heated to 150 ºC and 130 ºC following the same procedure as shown in Figure 4(b) and 4(c). It was observed that MWCNT-PEDOT:PSS polymer did not show any drift in its initial resistance value when heated to 190 ºC and cooled back to RT. Hence we concluded that MWCNT-PEDOT: PSS composite exhibit thermal stability up to 190ºC as at this temperature its heatingcooling profile was found reversible in nature as shown in Figure 4(d). On the other hand, a significant drift in the initial resistance value of the MWCNTPANI composite was observed even when heated to 150ºC and cooled back to RT (as shown in Figure 4(b)) while a negligible amount of drift was noticed when it was heated to 130 ºC as shown in Figure 4(c). Therefore it was concluded that MWCNT-PANI composite is thermally stable below 130 ºC only where it's heating– cooling profile was found to be reversible as shown in Figure 4(d).

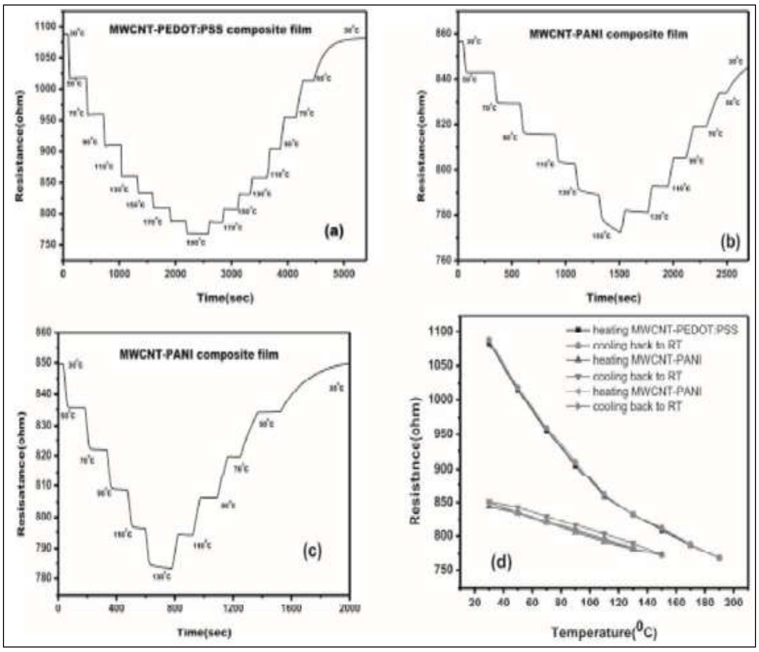

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Fig 4: Heating Cooling Profile in Step Sequence for (a) MWCNT-PEDOT: PSS Composite Film and (b), (c) MWCNT-PANI Composite Film (d) Heating-Cooling Profile Curve

The above results shows that MWCNT-PANI composite cannot be utilize in heat sensing applications because of its poor thermal stability where as MWCNT-PEDOT: PSS composite can be a suitable candidate for such applications. Hence MWCNT-PEDOT: PSS composite and PEDOT: PSS polymer was further investigated before its application as heat sensing device.

Thermal analysis studies of pedot: PSS polymer film

Further study was carried out to optimize the temperature below which the PEDOT: PSS polymer film exhibit thermal stability. The same heating procedure including heating to 190, 170 and 150°C in step sequence and then cooling down to room temperature was followed as shown in Figure 5 and corresponding heating–cooling profile was plotted (Figure 5(d)). The above results show

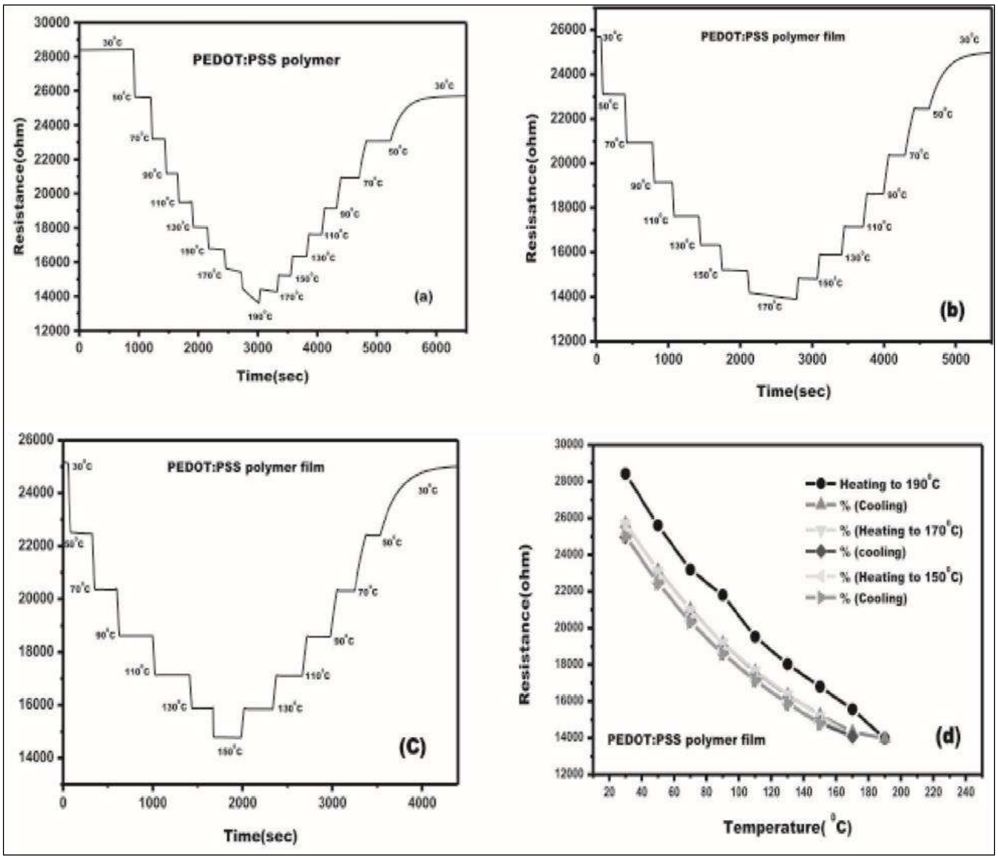

Fig 5: Polymer Heating-cooling Profile for PEDOT: PSS Polymer Film (a), (b), (c) in Step Sequence (d) Heating-Cooling Curve

Figure 5 (a) shows a large deviation of the cooling path when compared with heating path in the polymer film, implying significant degradation of the polymer at 190°C while the perfect reverse nature was observed in case of MWCNTPEDOT:PSS composite film at same temperature (Figure 4 (a)). This kind of behavior states that the addition of MWCNT in polymer imparts a large improvement in thermal stability over polymer film. These results demonstrate that MWCNTPEDOT: PSS has better thermal stability than the commercial PSS: PEDOT. Hence we conclude that (Figure 5 shows) that the PEDOT:PSS polymer exhibit thermal stability below 150°C as at this temperature the heating–cooling profile is reversible in nature although it is not the same with 170 °C and 190 °C.

Heat Sensor Analysis

All the electrical measurements were done using electrical characterization unit (Keithley 4200- SCS). PEDOT: PSS polymer film was tested for its heat sensing response in air atmosphere and it was found to exhibit excellent and repeatable response at 100ºC with fast and complete recovery as shown in Figure 6 (a). Figure 6 (b) shows the response of the polymer film when subjected to different temperatures as 100,120,150,180 ºC.

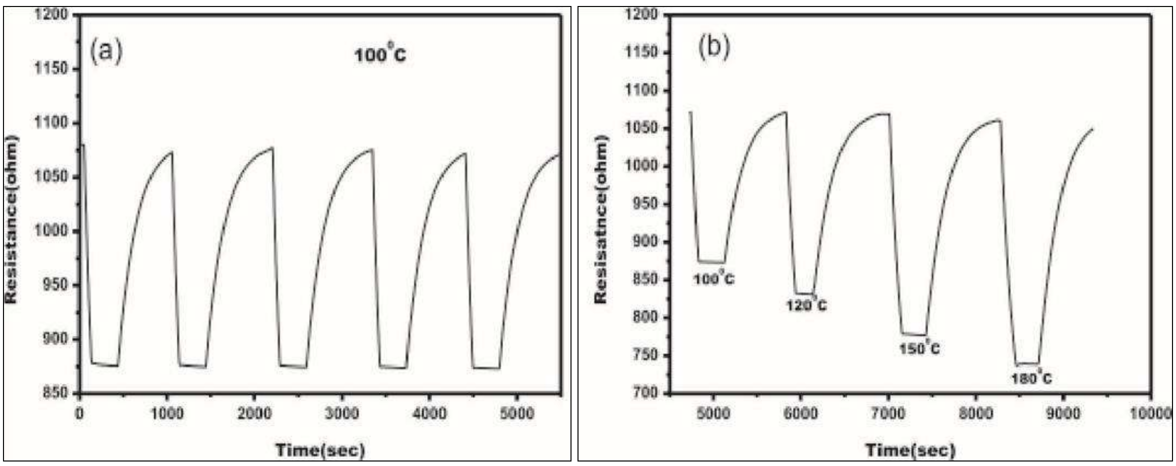

Fig 6: Response of the PEDOT: PSS Polymer at (a) 100 ºC (b) 100, 120, 150, 180 ºC

It was observed that PEDOT:PSS polymer showed complete recovery at 100 and 120 ºC without having any deviation from its initial resistance value while the same showed partial recovery with slight deviation from its initial resistance value when subjected to more than 150ºC as shown in Figure 6 (b).

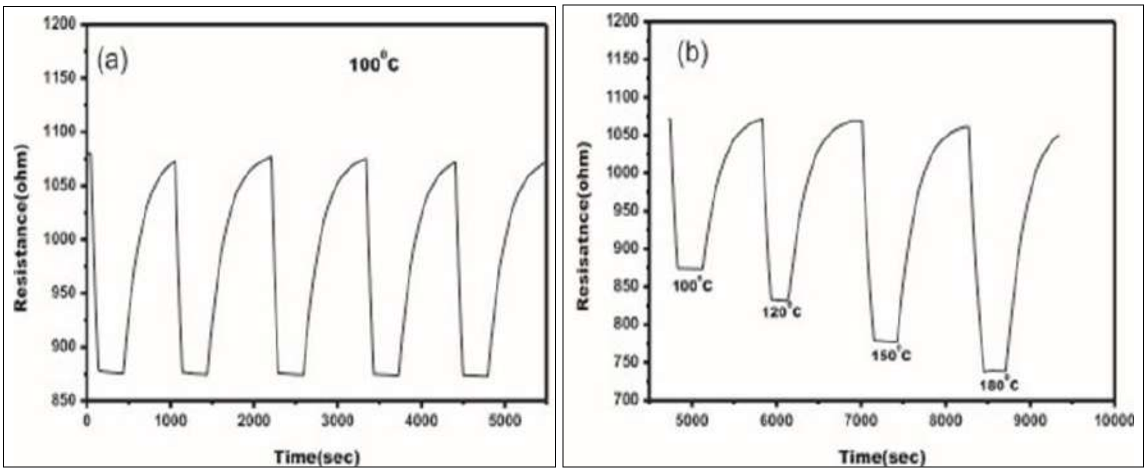

Fig 7: Response of the MWCNT-PEDOT: PSS Composite at (a) 100 ºC (b) 100, 120,150, 180 ºC

When compared with PEDOT: PSS polymer, MWCNT-PEDOT: PSS composite was found to exhibit better and improved response at same temperature of 100ºC as shown in Figure 7(a). Figure 7(b) demonstrated that MWCNT-PEDOT: PSS composite showed fast and complete recovery at 100,120,150 and 180ºC without having any significant deviation from its initial resistance value.

Conclusion

Two types of conducting polymer composites were fabricated, using poly (3, 4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT: PSS) and Polyaniline (PANI). A comparative temperature dependent resistance study was conducted where thermal stability behavior of these composites was investigated. MWCNT-PEDOT: PSS composite was found to have some merits over MWCNT-PANI composite such as superior thermal stability. Also when tested for heat sensor, PEDOT: PSS composite was found to exhibit excellent response, small response and recovery time, good repeatability and complete recovery when compared with PEDOT:PSS polymer. Hence it is concluded that MWCNTPEDOT: PSS composite is better candidate and promising material for heat sensing applications than PEDOT: PSS polymer MWCNT-PANI composite.

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