Dielectric, electric and thermal properties of carboxylic functionalized multiwalled carbon nanotubes impregnated polydimethylsiloxane nanocomposite

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Abstract. The dielectric, electric and thermal properties of carboxylic functionalized multiwalled carbon nanotubes (F-MWCNT) incorporated into the polydimethylsiloxane (PDMS) were evaluated to determine their potential in the field of electronic materials. Carboxylic functionalization of the pristine multi walled carbon tubes (Ps-MWCNT) was confirmed through Fourier transform infrared spectroscopy, X-ray diffraction patterns for both Ps-MWCNTs and F-MWCNTs elaborated that crystalline behavior did not change with carboxylic moieties. Thermogravimetric and differential thermal analyses were performed to elucidate the thermal stability with increasing weight % addition of F-MWCNTs in the polymer matrix. Crystallization/glass transition / melting temperatures were evaluated using differential scanning calorimeter and it was observed that glass transition and crystallization temperatures were diminished while temperatures of first and second melting transitions were progressed with increasing F-MWCNT concentration in the PDMS matrix. Scanning electron microscopy and energy dispersive x-ray spectroscopy were carried out to confirm the morphology, functionalization, and uniform dispersion of F-MWCNTs in the polymer matrix. Electrical resistivity at temperature range (100-300°C), dielectric loss (tanδ) and dielectric parameters (ε', ε'') were measured in the frequency range (1MHz-3GHz). The measured data simulate that the aforementioned properties were influenced by increasing filler contents in the polymer matrix because of the high polarization of conductive F-MWCNTs at the reinforcement/polymer interface.

1. Introduction
Polydimethylsiloxane (PDMS) has shown good flexibility, thermal stability, electrical resistance and dielectric strength due to the cross-linking density and degree of polymerization [1]. PDMS composites are used for the wide range of applications from sensor technology to radar absorbing materials [2, 3]. In addition, PDMS is used for substrate pattern transfer to various substrates due to its soft and flexible nature [4, 5]. During fabrication it leads to residual deformation, the large expansion coefficient of the polymer induces residual stresses in the polymer.

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This phenomenon causes misalignment of different structures. The misalignment of structure is usually resolved by incorporating fillers e.g. whiskers, nanoparticles and nano-tubes, etc [6, 7]. The highly conductive nano particles/tubes filled polymer matrix composites are a rapidly developing field in switchable and flexible microelectronics technology [8, 9]. The dielectric property of PDMS is modified by incorporating F-MWCNTs as nano filler in the PDMS matrix. Since carbon nanotubes (CNTs) possess large aspect ratio with extra ordinary thermal, mechanical & electrical properties; CNTs help in enhancing the thermal, mechanical and electromagnetic properties of the PDMS composite [10]. The focus of this research is on the fabrication of carboxylic functionalized multiwalled carbon nanotubes (F-MWCNT) reinforced in PDMS based composite. These PDMS composites are designed for high thermal stability and dielectric strength. When used as interconnects in semi-conducting devices, the conducting multiwalled carbon nanotubes (MWCNTs) can route electrical signals at speeds up to 10 GHz; this is usually attributed due to electron transfer over a wide range of length without intermediate interruption [11]. In this paper, Ps-MWCNTs are functionalized for uniform dispersion in PDMS matrix to study the effect on electric and thermal properties of the composite. The dielectric, electrical, morphological, spectroscopic and thermal analyses are performed and it is observed that all these properties are strongly influenced by increasing F-MWCNTs content in the polymer matrix.

2. Experimental

2.1. Materials
Ps-MWCNTs with 90% purity and average length and diameter were found to be around 30µm and 25nm were purchased from Nanoport. Co. Ltd, China. Room temperature vulcanized - polydimethylsiloxane was purchased from Wacker, Germany and it was used as received. Nitric acid, ammonium hydroxide and toluene were received from Merk. Polypropylene (PP) membranes with 0.2µm pore size were bought from Pall.Co., China.

2.2. Sample preparation

2.2.1. Surface modification of Ps-MWCNTs
To functionalize Ps-MWCNTs, purification was performed at 450°C with a temperature rise rate of 10°C per minute for 6 hours followed by their treatment with hydrochloric acid to remove metal traces, amorphous carbon and other impurities. In the second step, 2g purified MWCNTs were immersed in 68% conc. HNO₃ at room temperature. Then, the solution was sonicated in ultrasonicator bath at 40 KHz, 90°C for 4hours. Subsequently, the solution was washed with ultra-pure water five times and the pH of the solution was neutralized with ammonium hydroxide. The pH value was maintained at 5.5 and the solution was filtered with 0.2µm PP membrane. At the end, F-MWCNTs were collected by drying the nanotubes in the oven at 100°C for 12 hours. Functionalization mechanism is demonstrated in figure 1b.

2.2.2. Fabrication of F-MWCNTs based PDMS composite
The dispersion of Ps-MWCNTs in the polymeric systems is a difficult task. The carboxylic moieties make inter bond between multiwalled carbon nanotubes and polymer matrix. Initially, F-MWCNTs were dispersed in toluene using ultrasonication bath for 2 hours. This was followed by dispersion in PDMS using a mechanical stirrer at 5000rpm for 30 minutes. Furthermore, the F-MW with 90% purity and average length and diameter were found to be around 30µm and 25nm NT/PDMS solution was poured into the 6” x 6” x 2.5” mold. The pre-curing of F-MWNT/PDMS composite was carried out for 1 hour at 120°C and then temperature was raised to 160°C. The composite was kept at 160°C for 30 minutes. Dibenzoyl peroxide (0.2pphr) was used as a crosslinker for PDMS. Flow chart in figure 1b shows the route for the fabrication of the composite. Five different types of F-MWCNT/PDMS composites P0, P1, P2, P3, and P4 were fabricated keeping 0 ,0.1, 0.3 ,0.5, 0.7 wt% ratio of F-MWCNTs in PDMS matrix, respectively.
2.3. Characterizations

The spectroscopic characterizations of Ps-MWCNTs/F-MWCNTs were performed using Perkin Elmer Fourier Transformation Infrared (FTIR) spectrometer with KBr disc to study the functionalization and X-
Ray Diffraction (XRD) was done to confirm the crystalline nature of MWCNTs. Thermal properties of pristine/functionalized MWCNTs and PDMS composites were elaborated using Perkin Elmer Diamond thermal gravimetric/differential thermal analysis (TG/DTA). The isothermal crystallization (Tc)/glass transition (Tg) /melting (Tm) temperature responses of PDMS composites were investigated by using Perkin Elmer differential scanning calorimeter (DSC). The surface modification and dispersion of F-MWCNTs in the host polymer matrix were analyzed using scanning electron microscope along with the energy dispersive x-ray spectroscopy (SEM/EDS) Jeol JSM 6490 A. HP 4339B high resistance meter was used to measure the electrical properties with temperature augmentation. The dielectric parameters ($\varepsilon'$, $\varepsilon''$, tan$\delta$) were measured using the bridge LCR meter (Model HP 4284 A) and Agilent network analyzer.

3. Results and discussion

3.1. FTIR & XRD analysis of MWCNTs

Figure 2a represents FTIR spectra of Ps-MWCNTs and F-MWCNTs. The presence of the broad band in F-MWCNTs spectra in the range 2400-3500 cm$^{-1}$ confirms the presence of hydroxyl group and carboxylic group in KBr disc. The appearance of a peak approximately at 1450-1650 cm$^{-1}$ corresponds to the C–O stretching which indicates the introduction of carboxylic groups due to surface oxidation of nanotubes. The peak at 1100-1120 cm$^{-1}$ indicates a C–O vibration. The fingerprint region at 550-600 cm$^{-1}$ may indicate a bending vibration of C-H. Therefore, the spectrum clears the evidence for covalent attachment of organic moieties on the surface of F-MWCNTs.

Crystalline nature of F-MWCNTs is also confirmed from (10$^0$ to 80$^0$ (2$\theta$)) XRD pattern with a scanning step of 0.02$^0$/s; figure 2b shows the diffraction peaks at 26.71 and 44.91 corresponding to graphite structure derived from MWCNTs. Furthermore, the intensity of (002) and (100) peaks of F-MWCNTs are much closer to Ps-MWCNTs, provides the evidence for the fact that the treatment does not damage the graphene layer organization.

3.2. Scanning electron microscopy (SEM) and EDS analysis

SEM coupled with EDS was performed to investigate the morphology/compositional analysis of Ps-MWCNTs/F-MWCNTs. CNTs and composite samples were coated with gold to make them conductive for SEM analysis. The comparative analysis of Ps-MWCNTs and F-MWCNTs morphology was carried out as obvious in figure 3 at 50Kx magnification along with their EDS. Figure 3b confirms the oxidation of Ps-MWCNTs in EDS analysis. To analyze the dispersion of F-MWCNTs in the polymer matrix,
samples were broken in liquid nitrogen and then the cross-section of P3 (0.5wt% F-MWCNT/PDMS composite) was observed in SEM.

Figure 2b. XRD pattern for MWCNTs

Figure 3a. SEM images with EDS of Ps-MWCNTs

Figure 3b. SEM images with EDS of F-MWCNTs
Figure 4(a-b) shows the SEM micrograph of P3 (0.5wt% F-MWCNT / PDMS composite) at 50Kx and 90Kx magnification confirming the uniform dispersion of CNTs in the host polymer matrix. The uniform dispersion of F-MWCNTs in PDMS strongly influences the dielectric, electrical, structural and thermal properties of the polymer due to the strong interfacial interaction between polymer chains and nanotubes surface.

**Figure 4. SEM of F-MWCNTs reinforced polymeric composite at 50Kx (a) & at 90Kx (b)**

3.3. Thermogravimetric/differential thermal analysis (TG/DTA) of PDMS composites

TGA was used to determine the thermal degradation behavior of Ps-MWCNTs/F-MWCNTs and relative effect of different wt% loadings of F-MWCNTs in PDMS host matrix. Figure 5(a, b) represents the TGA and DTA traces between 25-800°C under the oxygen environment. The thermal properties of Ps-MWCNTs/F-MWCNTs and composites are also given in table 1. Thermal gravimetric analysis of Ps-MWCNTs (P6) and F-MWCNTs (P5) in figure 5a elucidate that P5 thermally degrade 13% in excess than P6 due to –COOH debonding from F-MWCNTs surface in the form of water vapors and CO₂ exhaust. The weight loss behavior of F-MWCNTs incorporated polymer composite is ranked as P4<P3<P2<P1<P0, as can be seen in figure 5a & table 1.

**Figure 5a. TGA of MWCNTs and PDMS nanocomposite**
This behavior defines the efficacy of increment of F-MWCNTs in PDMS polymer matrix. The nano scale interaction of F-MWCNTs with polymeric chains of host matrix causes the maximum thermal stability of the F-MWCNT/PDMS composites.

| Sample ID | % Wt Loss at 250°C | % Wt Loss at 375°C | % Wt Loss at 525°C | % Wt Loss at 800°C |
|-----------|--------------------|--------------------|--------------------|--------------------|
| P0        | 7.76               | 35.90              | 72.86              | 87.09              |
| P1        | 7.19               | 31.93              | 69.17              | 83.39              |
| P2        | 5.01               | 24.84              | 61.79              | 75.70              |
| P3        | 4.91               | 18.86              | 50.41              | 64.63              |
| P4        | 3.22               | 12.95              | 29.36              | 43.04              |
| P5        | 0.66               | 2.71               | 3.10               | 13.30              |
| P6        | 0.38               | 0.67               | 0.94               | 5.20               |

In conclusion, thermograms confirm that F-MWCNT/PDMS composites exhibit more thermal stability than pristine PDMS due to the heat quenching ability of F-MWCNTs as obvious in DTA thermograms. In DTA curves, it is clear that F-MWCNTs absorb more heat than Ps-MWCNTs due to bond cleavage of covalently attached moieties on the surface of MWCNTs. The DTA behavior of both polymer matrix and CNTs dispersed composites is completely endothermic but the polymer absorbed additional heat due to the presence of F-MWCNTs. Figure 5b illustrates the upward shift in thermograms which portrays that addition of F-MWCNTs enhance the thermal stability of the host polymer.

Figure 5b. DTA of MWCNTs and PDMS nanocomposite.

3.4. Differential scanning calorimeter (DSC) analysis

Figure 6 elaborates the DSC scrutiny obtained from pure PDMS and different wt% reinforced F-MWCNTs in PDMS after heating at a rate of 10°C/min from -165°C to 250°C. Crystallization temperature (Tc, Tc*) gradually decreases with the wt% increment of F-MWCNTs from 0.1% to 0.7% due to the reduction of spherulite sites in the polymeric composite [11]. The same behavior is revealed in the melting temperature (Tm, Tm*) response of the composite specimens.
Figure 6. DSC profiles displaying Tg, Tc, Tm of the PDMS nanocomposites

Figure 6 also simulates that glass transition temperature (Tg) of F-MWCNT/PDMS composite decreases with percent enhancement of F-MWCNTs because of the interaction of polymer chains with nanotubes through carboxylic moieties. The nano reinforcement improves the ductile/rubbery behavior of polymer matrix up to ~130°C. The reduction of Tc, Tg & and enhancement of Tm confirm the proficiency of functionalized nanotubes due to the intermolecular interaction between PDMS molecular chains and F-MWCNTs as evident from table 2.

Table 2. Table of DSC parameters.

| Sample ID | Tg (°C) | Tc (°C) | Tm1 (°C) | Tm2 (°C) | Tc* (°C) |
|-----------|---------|---------|----------|----------|----------|
| P0        | -121.37 | -93.23  | -74.84   | -45.25   | -51.90   |
| P1        | -122.19 | -93.23  | -74.93   | -47.56   | -54.34   |
| P2        | -125.56 | -96.60  | -73.93   | -47.80   | -55.72   |
| P3        | -129.66 | -98.24  | -73.11   | -42.79   | -55.99   |
| P4        | -134.67 | -99.88  | -72.66   | -43.61   | -56.90   |

3.5. Electrical, dielectric and microwave permittivity measurements

The dc electrical resistivity was measured in the temperature range 100-300°C using two probe resistivity apparatus. Standard Arrhenius equation [12, 13] was used to calculate dc-electrical resistivity (ρdc) for all fabricated composites. The dc electric resistivity with respect to temperature is represented by figure 7(a). It is observed that dc resistivity decreases with the increase in temperature which confirms the semiconducting behavior of fabricated composites. It is also observed that dc electric resistivity decreases with the increase in F-MWCNTs contents and minimum value is observed for 0.7 Wt% F-MWCNTs filled composite.
The dc electrical resistivity at 100°C was found in the range $0.1-1.25 \times 10^{12} \Omega \text{cm}$. The electrical resistivity data confirms that as F-MWCNTs wt % increases, the electric conductivity of fabricated composite increases. The accumulation of electrostatic charging, usually observed on insulating matrix surface leads to a serious problem and high electric conductivity above $\sigma=10^{-6}$ Sm$^{-1}$ is required. F-MWCNTs (highly electrical conducting nanofiller) were used to get a maximum value of electrical conductivity in the polymeric matrix. The dielectric constants ($\varepsilon'$) and dielectric loss ($\tan\delta$) of various filler concentrations with frequency, represented in figure 7 (b, c), and were calculated using standard relations [14].

**Figure 7a.** The dc electrical resistivity with temperature ($\rho_{dc}$).

**Figure 7b.** Dielectric parameters as a function of frequency ($\varepsilon'$) of nanocomposites
The value of both these of parameters was found in ranges 31-75 and 0.092-0.31 at 100Hz. This indicates that with the increase in nanotubes concentration, both of these parameters are influenced. The observed dielectric behavior in fabricated composites is due to the shift in electric charges from their mean or equilibrium position between the PDMS/F-MWCNT interfaces. Furthermore, the wt% increase in F-MWCNTs results in heterogeneous phases having different polarizability, which in turn leads to accumulation of different charges at interfaces. As a result, these parameters decrease with the increase in frequency [15, 16]. The effect of microwave frequency on dielectric parameters was measured in the frequency range (1MHz-3GHz).

The behavior of dielectric parameters at frequency range 0 to 3GHz for P0-P4 is represented in figure 8 and 9. The effective decrease in measured values is observed for both of these parameters at 1GHz. The permittivity originates at the interface of composites due to the orientation polarization, space charge induced polarization, electrostatic and electronic polarization. The polarization is influenced by resonance generated at the expanse of higher frequencies, especially at microwave frequency range leads to electronic polarization at interfaces [17]. The negative values of permittivity for composites are attributed by quantum dot excitation at interfaces explained theoretically [18].

![Figure 7c. tanδ as a function of frequency of nanocomposites.](image)

![Figure 8. Dielectric loss at microwave frequency range (1MHz-3GHz) of fabricated F-MWCNT/PDMS](image)
Figure 9. Permittivity of all F-MWCNT/PDMS composite at microwave frequency range (1MHz-3GHz)

4. Conclusion
The wt% increment of the nanotubes contents in PDMS matrix influences and improves dielectric/electrical & thermal behavior of fabricated PDMS/F-MWCNT composites. The remarkable enhancement in thermal stability and heat quenching capability of PDMS with the incorporation of F-MWCNTs are clearly observed in TG/DTA. The reduction of Tc & Tg, and improvement in Tm are augmented by DSC analyses. The uniform dispersion of F-MWCNTs in PDMS is obvious from the SEM images. XRD results corroborate that crystalline nature does not change with the carboxylic functionalization of Ps-MWCNTs. The effective increase is observed in dc electric conductivity with% increase in nanofiller content. The decrease in electric resistivity by temperature and dielectric parameters with frequency confirmed the semiconducting behavior of fabricated composite. The dielectric parameters are influenced with increasing F-MWCNTs incorporation in PDMS due to the interface polarization between the filler and matrix. These polymeric composites are resonated due to atomic, electrostatic and electronic polarization at 3GHz.

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