



Towards High Temperature Applications of Carbon Nanotubes (CNTs) [I]: Effect of Surface Activation on Pristine carbon nanotubes (pCNTs)

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ABSTRACT

Due to its exceptional physical, mechanical, electrical and thermal properties, CNTs are employed as fillers in composites to confer these intrinsic characteristics in the resulting CNTs based composites in automotive, microelectronics, sports, coating and films and energy storage industries. Yet, for CNTs based composite, potential application is envisioned in high temperature application such as heat engines, gas turbines, reactors, space vehicles, etc. Therefore, the present research would demonstrate the effect of surface activation on the pristine carbon nanotubes (pCNTs); on the route to ascertain the potential of high temperature application of CNT. Such aspects as functionalization of as-received pCNTs and characterizations; Fourier-transform infrared spectroscopy, Raman spectroscopy, Thermogravimetric analysis and Differential scanning calorimetry of the pristine and functionalized CNTs are explained. The significance of functionalization in temperature stability and in the formation of a stable suspension of CNTs/polar solvents is explored.

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INTRODUCTION

Carbon nanotubes (CNTs) have been identified as a potential material in numerous applications, ranging from safety to energy. However, poor dispersion/solubility in aqueous and organic solvents has limited the use and applications of carbon nanotubes; this could be attributed to the high rigidity, chemical inertness and strong π - π interactions of nanotubes (Norizan et al., 2020). As-produced CNTs (pristine) are bind together in bundles or entanglements containing of 50 to a few hundred individual CNTs by van der Waals force; these bundles/agglomerates reduced mechanical and electrical properties of composites as compared with theoretical predictions related to individual CNTs (Rubel et al., 2019; Sabet et al., 2018). In essence, dispersion of CNTs is not a geometrical problem alone, involving length and size of the CNTs, rather it relates to a method on how to separate individual CNTs from CNT agglomerates and stabilize them in matrix to avoid secondary agglomeration. Hence, the side walls of CNTs must be chemically modified (functionalized) to enhance their dispersion/solubility in solvents or matrices. Functionalization could be achieved via chemical (Maity et al., 2020),

electrochemical (Quintero-Jaime et al., 2020), mechano-chemical (Nakonechna et al., 2018) and plasma treatment. Chemical functionalization; commonly referred to covalent functionalization uses primarily strong acids (oxidation) to covalently add oxides groups such as carboxylic acids, carbonyl and hydroxyl to the tube ends and defect sites of CNTs (Singh et al., 2016). Then, additional chemical reactions could be carryout on these oxides groups to covalently functionalize with groups such as amides, thiols, etc. (Afrin & Shah, 2015; Ajori et al., 2015; Janudin et al., 2018).

The covalent functionalization critically altered the inherent properties of the CNTs; changed the electrical conductivity, thermal properties, and may shorten the length of nanotubes. Generally, the present of carboxylic, hydroxyl, polymer, and other hydrophilic groups assist in enhancing the chemical structure of CNTs by filling the defect sites, hence improving the conductivity and charge transfer (Norizan et al., 2020). CNTs are potential candidates for different applications. For instance, the large surface area and aspect ratio (L/D) are ideal for biomedical applications; drug and enzyme delivery. Thermal stability, high thermal conductivity, and large current



capacity properties are good for interconnect applications. To explore internal properties of CNTs, several techniques use the optical response such as infrared spectroscopy, Fourier transform infrared and Raman spectroscopy. The novelty in my study is in the temperature range; sintering temperature of the traditional silica (an intended matrix, 1450oC) and the heating atmosphere; air, to which the pristine and the functionalized carbon nanotubes were subjected.

MATERIALS AND METHODS

Materials

Carbon nanotubes (multiwalled, hydrophilic, 10-20 nm outer diameter OD, 5-10 nm inner diameter ID, 10-20 μm length, > 150 m²/g special surface area SSA, % Purity > 98%, CVD-grown) was received from Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences (Sichuan Sheng, China). Sulphuric acid 95-98 % A.R/ACS; for activating the pristine multiwalled carbon nanotubes (pMWNTs) were obtained from Ever Gainful Enterprise Sdn Bhd (Subang, Selangor, Malaysia).

Preparation/characterization of CNTs

Functionalization of pCNTs

100 mg of the pCNTs were acid treated with 100 ml of 6M H₂SO₄. The mixture was then ultra-sonicated using water bath sonicator for 4 – 6 hours at 60oC. After sonication, the residue was decanted and successively washed with distilled water in a centrifuge at 8000 rpm for 30 seconds. Finally, the as-washed residue was dried in an oven at 80 – 100oC for 24 hours. The procedure is similar to what have been described in earlier studies by Tijjani et al. (2019) & Tijjani and Nasir (2019).

Dispersion of the functionalized CNTs

Both pCNTs and activated CNTs were dispersed in distilled water and ethanol by ultrasonication employing varied sonication/dwelling time (10, 20, 30, 60, 90, & 120 minutes/day) to unbundle the CNTs so that the optimum condition as per time and dispersion medium would be established.

Characterization of CNTs

The following analyses were carried out on the pristine and functionalized CNTs: Fourier-transform infrared spectroscopy (FTIR), Raman Spectroscopy, Thermogravimetric

analysis (TGA), Differential thermogravimetric analysis (DTG) and Differential scanning calorimetry (DSC).

a. Fourier-transform infrared spectroscopy analysis

The FTIR study was carried out to ascertain the presence of carboxylic functional groups in the resulting activated CNTs. The Infrared (IR) spectra were acquired by Perkin Elmer spectrum 100 series Fourier Transform Infrared Spectrophotometer in the frequency scan range of 4000 – 650 cm⁻¹. Powdered samples of pristine/functionalized CNTs were subjected to this analysis.

b. Raman spectroscopy

The graphitizations of the pristine and activated CNTs were obtained by Raman spectroscopy in domain wave number of 0 – 4200 cm⁻¹.

c. Thermogravimetric analysis/Differential scanning calorimetry

The experiments were performed in an alumina ceramic pan (70 μl) bearing a sample with an average mass of 2 mg from room temperature (25oC) to 1450oC, in oxidizing (air) atmosphere with a flow rate of 50 ml/min. The mass-change (TG) and its first derivative with respect to time (DTG) were deconvoluted in Gaussian functions and plotted as a function of the temperature. TG and DTG graphs were obtained for the pristine/functionalized CNTs. The TGA/DSC machine was made to carry out both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

With Differential Scanning Calorimetry (DSC) using TGA/DSC analyzer, approximately, 2 mg of the pristine and oxidized CNTs each were placed in an alumina ceramic pan, purged under air with heating rates of 20 °C/min at 50 ml/min.

RESULT AND DISCUSSION

Preparation/structural characterization of MWNTs

1. Identification of functional group of CNTs by Fourier-transform infrared spectroscopy

Figure 1, compares the Fourier-transform infrared spectroscopy spectra of pristine and functionalized carbon nanotubes in a range of 400 – 4000 cm⁻¹. A weak band at 2912 cm⁻¹ which is a characteristic of alkane group appeared on the surface of the pristine with two similar peaks at around 2913 and 2844 cm⁻¹ (Chiang et al., 2011; Figueiredo et al., 1999) absorbed on functionalized carbon

nanotubes with higher intensities, signified better stability of functionalized tubes than the pristine. The bands in 1300 – 950 cm^{-1} range at the lower wavenumbers for the pristine spectrum (not shown by numbers), proved the presence of C – O bond. Some of these peaks can be seen on the surface of functionalized CNTs, additionally, the appearance of 1704 and 1733 cm^{-1} due to the C=O stretching vibration indicate the presence of carboxylic acid group attached during the functionalization/oxidation of the CNTs (Chiang et al., 2011; Malikov et al., 2014; Silverstein et al., 2005). Hence, the implication of decoration of the surface of hydrophobic CNTs with the carboxylic functional group to hydrophilic CNTs as confirmed by Fourier-transform infrared spectroscopy is the surface activation of the nanotubes which facilitates bonding with polar solvents and subsequent homogeneous dispersion of the tubes in the solvents to a stable dispersed homogeneous suspension.

basic like peaks; D band (referred to as disorder induced peak), G band (called graphite band), and G' band (Dresselhaus et al., 2010).

The D band observed at about 1340 cm^{-1} stands for scattering from defect and amorphous carbon impurities or sp^3 hybridized carbons in the carbon nanotubes walls which signify the high-density zone-edge state phonons (Chieu et al., 1982; Nemanich and Solin, 1979). The G band at approximately 1570 cm^{-1} is related to E_{2g} graphite mode indicating highly ordered frequency in-plane stretching vibration of C-C bonds or tangential stretching of the sp^2 -bonded carbon atoms in the graphene-like structure, which are attributed to defect-free carbon nanotubes. The G' band around 2670 cm^{-1} is due to the double resonance process which does not account for elastic defect related scattering and is a characteristic band for defect-free sp^2 carbon. The ratio between D band and G band intensities represented as I_D/I_G is proportion to

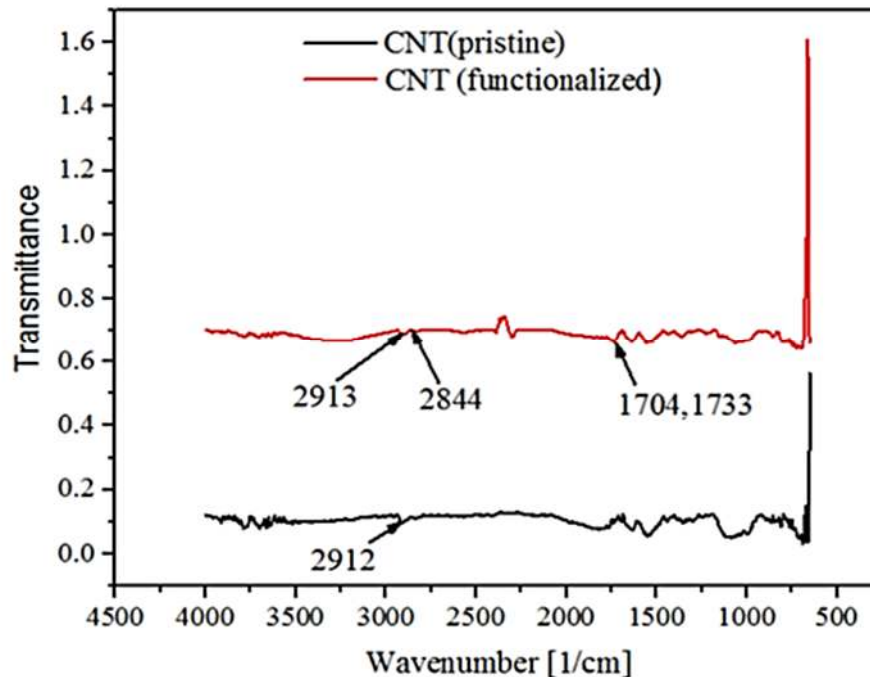


Figure 1: Fourier-transform infrared spectroscopy spectra of pristine and functionalized CNTs.

2. Raman spectroscopy of CNTs

The Raman spectra, comparing the pristine and functionalized CNTs are depicted in Figure 2. Each spectrum is comprising of three

the extent of defect incurred on the surface of carbon nanotube and could be used to quantify the oxidation process on the nanotubes (Malikov et al., 2014). As calculated from Figure 2, the ratios (I_D/I_G) are 0.84 and 0.94 for the

pristine and functionalized CNTs respectively. Accounting for approximately 12% defects increment as a result of surface functionalization of the pristine to functionalized CNTs. This result is consistent with 12 % increment as reported by the previous researchers (Singh et al., 2013) and they attributed the significant increment to perhaps generation of carboxyl sites on the treated carbon nanotubes (Edwards et al., 2011; Zhang et al., 2002). Also the slight increase in tangential mode frequency from 1577 cm⁻¹ of the pristine to 1582 cm⁻¹ of the functionalized CNTs ($\Delta t = + 5$ cm⁻¹), suggests changes in the CNTs chemical structure (Rao et al., 1997), for instance change in the type and amount of chemical functional groups attached to CNTs surfaces (Chiu et al., 2002). Also, the changes could be increased in oxygen content in the carbon nanotubes framework that behaves as a

630oC or from about 550oC to 630oC for oxidized CNTs which are more thermally stable. Mass loss below 150oC is attributed to water loss and between 150oC to 400oC is related to carboxyl group degradation. At a temperature greater than 400oC, the weight loss is associated with the burning of oxygen atoms tightly bonded to the surface of the CNTs or amorphous carbon species (Figueiredo et al., 1999). Precisely, for both pristine and functionalized CNTs up to a temperature below about 520oC, there is no significant mass loss with functionalized CNTs being more stable than the pristine. This signifies the absence of significant amount of amorphous carbon in both the pristine and functionalized CNTs with functionalized being purer than pristine. This could be attributed to the oxidation process of pristine to functionalized CNTs which highlight the importance of sulphuric acid apart from

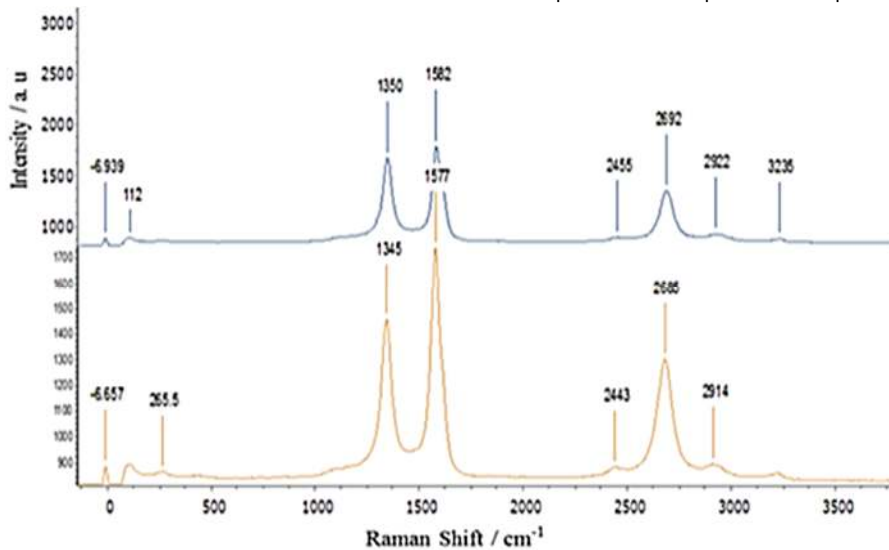


Figure 2: Raman spectra of pristine (Upper) & functionalized CNTs (Lower)

p-type dopant.

3. Thermogravimetric analysis of CNTs

To determine the thermal stability and /or to find the best condition for oxidation of carbon nanotube with minimum structural defects, TGA was employed. Figure 3, demonstrate the mass loss (%) as a function of the temperature of the pristine and functionalized carbon nanotubes heated from room temperature to 1450oC. The decomposition or degradation of the pristine occurred in one step from about 530oC to

decorating the surface of CNTs with the carboxylic functional group; it further purified the nanotubes from non-graphitic carbonaceous species. The residual percentages of pristine and functionalized CNTs after heating to 1450oC in atmospheric air as depicted in Figure 3, are 1 wt. % and 4 wt. % respectively. This finding justifies the importance of functionalization of CNTs prior to exploitation for various applications.

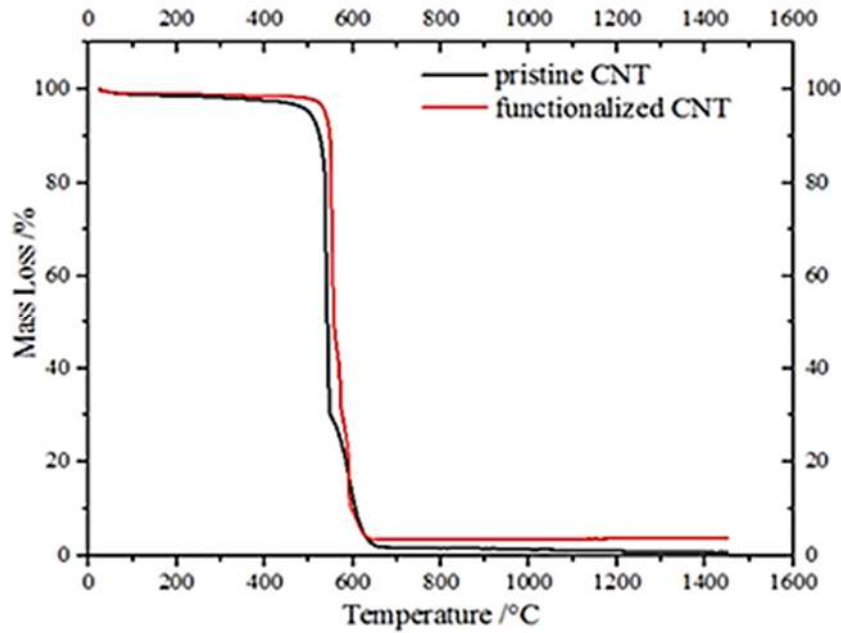


Figure 3: Thermogravimetric analysis profile of pristine & functionalized CNTs showing percentage mass loss (in air) as a function of temperature

4. Differential thermogravimetric analysis (DTG) of CNTs

The Differential thermogravimetric analysis curves were shown in Figures 4 & 5, of pristine and functionalized CNTs heated from room temperature up to around 700°C. For the pristine, it can be seen that the degradation or

decomposition of the nanotubes occurred in two steps as depicted in Figure 4, by two strong and weak bands at approximately 530°C and 600°C, respectively. Also, a more stable thermal degradation occurred in three steps for functionalized CNTs at about 560°C (strong and narrowed up band), and two weak bands at around 580°C and 600°C as shown in Figure 5.

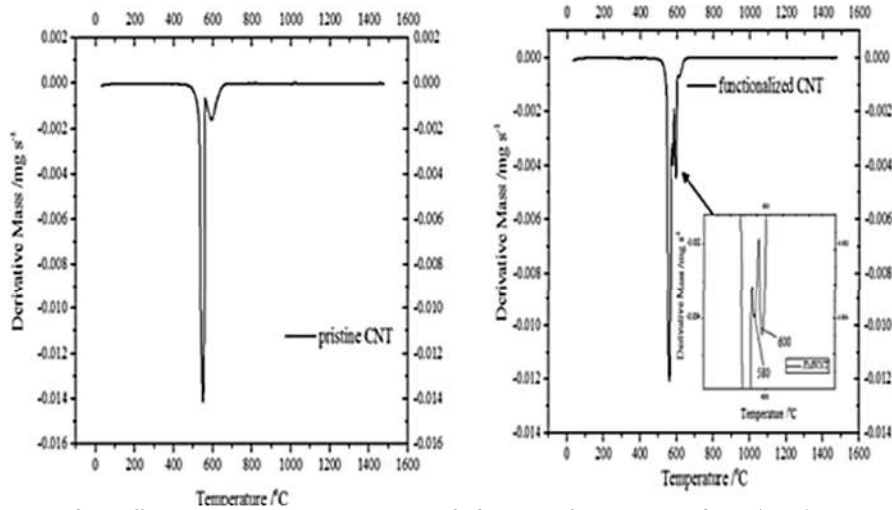


Figure 4 & 5: Differential thermogravimetric curve of pCNTs and functionalized CNTs (in air) respectively as a function of temperature

Most of the CNTs in functionalized carbon nanotubes have similar structures with functionalized groups on the surface as narrow degradation peaks.

Differential scanning calorimetry of CNTs

In a similar profile to Differential thermogravimetric curves of pristine and functionalized CNTs, Figures 6 & 7 demonstrate the differential scanning calorimetry curves for pristine and functionalized CNTs respectively; heated from room temperature to 1450°C. For the pristine CNTs, there are two exothermic transition peaks at approximately 530°C (strong and narrowed band) and 600°C (weak band) as shown in Figure 6. These peaks are attributed to thermal degradation of the pristine. Also, for oxidized CNTs as depicted in Figure 7, three exothermic transition peaks at approximately 560°C, 580°C and 600°C are due to the thermal decomposition of CNT. Hence for both pristine and functionalized CNTs profiles, there is no peak associated with amorphous phase burning. This further confirms the purity of both the pristine and functionalized CNTs.

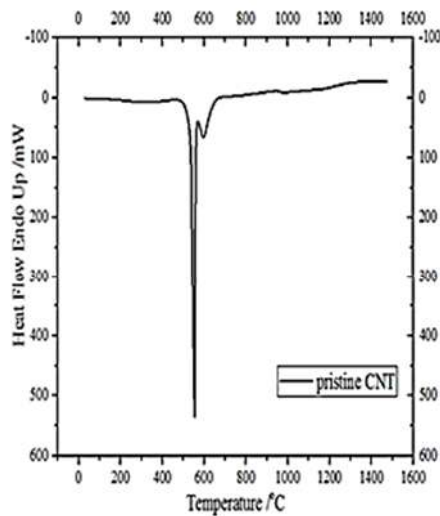


Figure 6

ethanol. For functionalized CNTs, ultrasonicated for 30 minutes/day in ethanol a stable suspension of CNTs/ethanol was obtained which remain stable for > 24 weeks (Figure 8(a)). The same result was obtained for functionalized CNTs dispersed in distilled water for 120 minutes/day (Figure 8(b)). Whereas, the pristine CNTs in both distilled water and ethanol at all the experimented time/day separate out into two distinct mixtures of CNTs in distilled water and ethanol (Figures 8 (c) & (d)).

This phenomenon can be explained on the account of the presence of organic function groups on the defected surface of functionalized CNTs. The interaction among the nanotubes floss after the de-bundling process (ultrasonication) and the improved polarity due to oxidation of the tubes (by mild acid treatment) have resulted in the enhanced dispersion of functionalized CNTs in polar solvents to obtain the stable dispersed suspension. The functional group (O-H) in ethanol and distilled water made a hydrogen bond with carbonyl (C=O) functional group that has been attached to the outer wall surface of functionalized CNTs. Similar

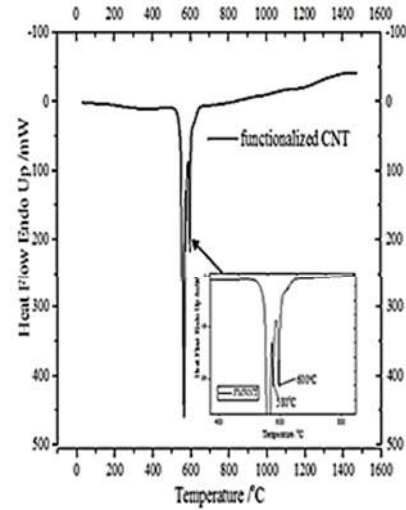


Figure 7

Figure 6 & 7: Differential scanning calorimetry curve of pCNT and functionalized CNT (in air) respectively as a function of temperature

Dispersion test

As obtained from the results, ultrasonication for < 30 minutes and left for a day (<30 minutes/day) resulted in an immiscible mixture of each of the pristine and functionalized CNTs in both distilled water and

argument was mentioned by Aziah Buang et al. (2012), for functionalized multi-walled carbon nanotubes dispersed in acetone.

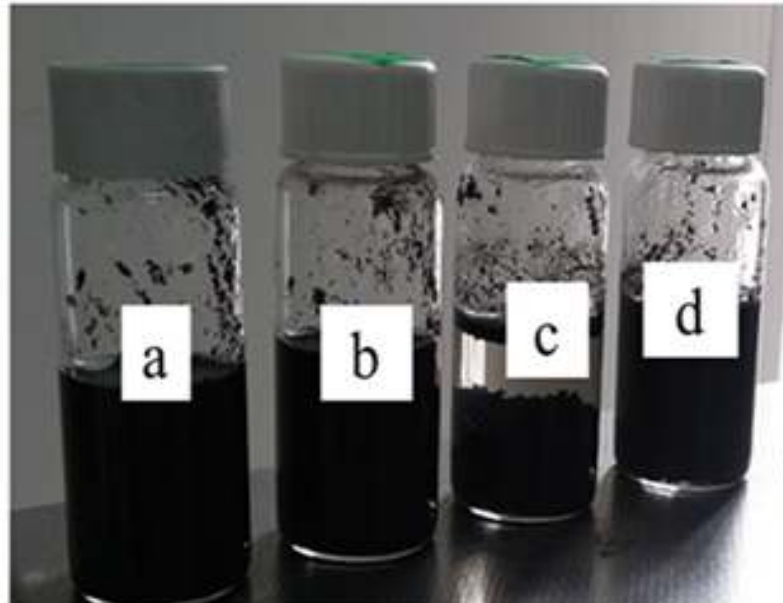


Figure 8: a) Functionalized CNTs in ethanol, b) functionalized CNTs in distilled water; – soluble after 30 & 120 min respectively; stable > 24 weeks, c) pristine CNTs in distilled water, d) pristine in ethanol; – immiscible mixtures

CONCLUSION

Microstructural characterization using Fourier-transform infrared spectroscopy, Raman spectroscopy, Thermogravimetric analysis, Differential Thermogravimetric analysis and Differential scanning calorimetry verified the surface activation, structural integrity, extent of thermal stability/purity of the pristine and functionalized CNTs. These techniques have ascertained the effectiveness and degree of acidic oxidation/functionalization of pristine to oxidized CNTs. The functionalized CNT emerges as the best candidate in terms of thermal stability and in the preparation of a stable dispersed suspension. This can be attributed to better surface modifications in oxidized CNTs (due to oxidation process) than the pristine CNTs (as-received from the manufacturer).

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