



# High performance natural rubber composites with conductive segregated network of multiwalled carbon nanotubes



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## ABSTRACT

Multiwalled Carbon nanotubes (MWCNTs) were covalently functionalized by H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> treatment to produce Carboxylated Multiwalled Carbon nanotubes (MWCNTR). Presence of carboxyl moieties on MWCNT were confirmed by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Thermo gravimetric analysis (TGA). These hydrophilic polar groups helped in getting stable aqueous dispersions of nanotubes. High performance composite with good mechanical and electrical properties was prepared by ultrasonication assisted mixing of aqueous dispersions of MWCNTR with natural rubber (NR) latex followed by film casting and curing. A segregated network of nanotubes was formed along the boundary of latex spheres even at low concentration which is evident from very low percolation threshold (0.086 vol%), high conductivity and dielectric constant. The network formation was confirmed by TEM and supported by strain sweep studies. The tensile strength increased by 61%, tensile modulus by 75% and tear strength by 59% by the addition of 0.5 parts per hundred rubber (phr) MWCNTR. The inclusion of 1.0 phr MWCNTR in the NR matrix increased the dielectric constant from 4.7 for pure NR to 918 at 100 Hz. The AC conductivity reached a value of 10<sup>-4</sup> S/m for the nanocomposite. This nanoscale, flexible, reinforced natural rubber based composites with high dielectric constant and conductivity could find application as electromagnetic wave absorbers in the low frequency region.

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## 1. Introduction

Carbon nanotubes (CNTs) have been extensively used as a reinforcing and electrically conductive nanofiller in the preparation of polymer nanocomposites. Combination of unique mechanical, electrical and thermal properties of CNTs with flexibility and easy processability of polymers facilitate many applications such as strong light weight automotive parts, sporting goods to boat hulls, supercapacitors, actuators and electromagnetic shields [1]. Effective and uniform distribution of CNTs in the polymer matrix plays a major role in the achievement of percolative network formation at low filler loadings. If the entire volume of fillers can participate in a conductive network, percolation can be achieved at low filler loading. There are reports on segregated network composites containing conductive fillers like carbon black, CNTs and graphene in which the fillers are oriented along the boundary between the polymer matrix particles to form a segregated

network instead of being randomly distributed in the system [2–8]. These composites have lower percolation threshold compared to composites with randomly distributed conductive fillers as the fillers are oriented along a specific path around polymer particles and can easily form a conductive network at low weight fractions. The studies also claim that the formation of CNT network in the polymer matrix improve mechanical and electrical properties.

Bhattacharyya et al. [9] have reported reinforcement of NR by networking of activated CNTs with the aid of sodium dodecyl sulphate. They have reported a percolation threshold of 0.4 vol%. In our work we aim to prepare natural rubber composite with a segregated MWCNTR network, having very low percolation threshold, high dielectric constant and good mechanical properties without using any surfactant.

In the present study acid treatment of MWCNT was done to introduce carboxyl moieties on CNT in order to get a stable aqueous dispersion. To ensure lower electrical percolation threshold with segregated nanotube network, composites were prepared by mixing the nanotube dispersion with compounded NR latex under

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ultrasonication followed by film casting. Mechanical properties, fracture surface morphology and microstructure of the composites were studied. Frequency dependence of dielectric properties and electrical conductivity were analysed. Electrical percolation threshold was determined using linear power law and the relationship between the microstructure and properties were investigated.

## 2. Experimental

### 2.1. Materials

MWCNT synthesized by Chemical Vapour Deposition (CVD) method having purity >95%, diameter <10 nm and length 5–15  $\mu\text{m}$  were used in this study. It was supplied by Shenzhen Nano Technologies Port Co. Ltd., China. AR grade  $\text{H}_2\text{SO}_4$  (98%) and  $\text{HNO}_3$  (69%) were purchased from Merck Specialties Private Ltd., Mumbai, India. Centrifuged NR latex of dry rubber content (DRC) 60% was purchased from Njavalli latex, Kochi, India. Rubber compounding chemicals used were of commercial grade.

### 2.2. Acid modification of MWCNT

1 g of the as received MWCNT was mixed with 200 ml of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture (3:1). The mixture was ultrasonicated in a bath (42 kHz) for 1 h and refluxed at 100 °C for 30 min. The mixture was cooled, diluted with water and filtered through PTFE membrane and washed with water till neutral. The solid was dried under vacuum and labelled as MWCNTR.

### 2.3. Preparation of NR–MWCNTR nanocomposites

The NR–MWCNTR composite with segregated network of nanotubes was prepared by ultrasonication assisted latex mixing and film casting method. The MWCNTR aqueous dispersion was prepared by sonicating aqueous suspension of modified nanotubes for 30 min and the dispersion was mixed with the compounded NR latex (as per formulation in Table 1) at various MWCNTR concentrations ranging from 0.05 to 1.0 phr in NR, and sonicated again for 30 min so as to achieve uniformity. The samples were kept overnight for maturation and then cast onto flat glass trays to get films. These films were dried at room temperature and then cured at 100 °C for 1 h in an air oven.

### 2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) characterization was done using Thermo Nicolet, Avatar 370 model IR spectrometer. Raman spectra of MWCNT and MWCNTR were recorded with Horiba Jobin Yvon Lab Ram HR system at a resolution of 2  $\text{cm}^{-1}$  by using excitation of 514.5 nm by Argon ion laser. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra X-ray photoelectron spectroscope (UK) with Al  $K\alpha$  radiation of 1486.6 eV.

**Table 1**  
Compounding formulation for NR latex.

Ingredients	Amount (g)
Centrifuged latex (60% DRC)	167.0
10% KOH solution	1.0
10% Potassium oleate solution	1.0
20% Vulcastab VL <sup>a</sup> solution	1.0
50% ZnO dispersion	1.0
50% ZDC dispersion	2.0
50% Sulphur dispersion	3.0

<sup>a</sup> Polyethylene oxide condensate.

The surface morphology of MWCNTRs and NR–MWCNTR composites were examined using a scanning electron microscope (SEM) JEOL Model JSM.6390 LV. The transmission electron microscopy (TEM) observations were made on a JOEL 3010 microscope. Thermogravimetric analysis (TGA) was carried out ranging from 30 °C to 700 °C at a heating rate of 20 °C/min with a TGA Q 50 Thermal Analyser (TA Instruments).

The tensile test was done on dumb-bell shaped specimens using Universal Testing Machine (10 kN), Shimadzu Autograph AG-I series with a grip separation of 40 mm as per ASTM D 412-06ae2. Tear strength was determined by ASTM D 624-00(2007).

The strain-amplitude dependent dynamic mechanical properties of the vulcanizates were measured at room temperature by means of a dynamic mechanical analyzer (Model Q 800, TA instruments). For this experiment tension mode was selected for the variation of the strain amplitude from 0.01% to 40% at 1 Hz frequency.

Dielectric and AC conductivity studies in the frequency range 40 Hz to 30 MHz were done using Precision Impedance Analyser (Agilent 4294A) at room temperature. DC electrical conductivity measurements were done by a standard two-probe electrode using a Keithley 2400 source-measure unit at room temperature.

## 3. Results and discussion

### 3.1. Structure of modified MWCNT

Acid treatment introduces polar carboxyl groups which is evident from IR peaks of O–H and C=O stretch at 3462 and 1710  $\text{cm}^{-1}$  respectively in Fig. 1(a). Raman spectra of both MWCNT and MWCNTR (Fig. 1(b)) consist of three characteristic bands, namely the D-band at 1320  $\text{cm}^{-1}$ , the G-band at 1572  $\text{cm}^{-1}$  and the D' band (shoulder in G) at 1602  $\text{cm}^{-1}$ . D\* band which is second order overtone band occurs at 2688  $\text{cm}^{-1}$ . Usually the intensity ratio of D to G ( $I_D/I_G$ ) is taken as a measure of concentration of defects. Because introduction of functional groups results in enhancement in the intensity of disorder induced D band. According to Murphy et al. [10] in order to get reliable information about the defect density it is necessary to include the intensity of the second order overtone mode D\*, which is due to two phonon processes and hence to first approximation independent of defect concentration. In this study  $I_D/I_G$  value decreased from 1.01 to 0.89 after acid treatment which is controversy to earlier reports in which the ratio increases upon covalent functionalization of nanotubes [11,12]. This may be due to the presence of impurities in the form of amorphous carbon and nano graphitic particles in pristine CNTs. Fig. 1(b) inset shows the variation of  $I_D/I_{D^*}$  and  $I_G/I_{D^*}$  for MWCNT and MWCNTR. Both ratio increases significantly for MWCNTR compared to MWCNT, which confirms the presence of increased number of  $\text{sp}^3$  hybridized carbons (disorder due to carboxylation) in the nanotube framework due to acid treatment.

XPS provide useful information about the functional groups and presence of defects on the nanotube surface. Fig. 1(c) shows deconvoluted C1s peak of MWCNTR from XPS. The main peak at 284.1 eV confirms the graphitic structure of MWCNTR [13]. Peak at 285.1 eV shows the presence of defects on the nanotube surface, whereas the peaks at 287 and 288.6 eV, represent carbon atoms bonded to different oxygen-containing moieties [14]. These hydrophilic groups interact favourably with water and create the electrostatic stability required for a colloidal dispersion as shown in Fig. 1(c) inset.

The thermograms of the as-received and oxidised MWCNT samples are presented in Fig. 1(d). Thermal degradation from 150 to 350 °C can be explained in terms of the removal of carboxyl groups and from 350 °C to 500 °C can be attributed to the elimination of hydroxyl functionalities from the surface of MWCNTR.

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