

Effect of Functionalization of MWCNT on the Conductivity and Percolation Threshold of CNT- Polymer Composites

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Abstract — The chemical functionalization of CNTs is a well known approach to control and engineer the interface and has been a subject of several research groups. It has been shown that unless the interface between nanotube and polymer is carefully engineered, poor load transfer between nanotubes, when in bundles, and between nanotubes and surrounding polymer chains may result in interfacial slippage in the process of preparing CNT-Polymer composites. In the present work we have functionalized MWCNT with –OH, –COOH and –S-O functional groups and then composites of above functionalized MWCNT were prepared with PMMA polymer. SEM imaging of functionalized MWCNT were done to see the structural changes before preparing composites. Conductivity measurements have been done on these composite specimens and results are analyzed to conclude the effect of functionalization of MWCNT. It is concluded that well dispersed CNT fillers result to lower percolation and higher conductivity is not substantiated for the COOH functionalized filler MWCNTs. The COOH-MWCNTs are best dispersed among the three functionalizations studied in this work but of lowest conductivity and largest percolation threshold. A perfect dispersion state of CNTs leads to individual CNTs separated in the matrix, and therefore, a higher percolation threshold. Higher dispersion alone does not translate to higher conductivity.

Keywords: MWCNT, CNT- Polymer Composites

I. INTRODUCTION

The enhanced reinforcement of Polymers by CNT fillers by controlling the interfacial properties has been well recognized and widely practiced and there is enough literature that substantiates to this fact [1]. The chemical functionalization of CNTs is a well known approach to control and engineer the interface and has been a subject of several reviews [2] – [6]. It has been shown that unless the interface between nanotube and polymer is carefully engineered, poor load transfer between nanotubes, when in bundles, and between nanotubes and surrounding polymer chains may result in interfacial slippage [7] and as such this effect clearly is detrimental to the properties of CNT – Polymer composites. On the other hand improved mechanical properties by controlled interface strategy have also shown to enhance the electrical conductivity [2] – [6]. The conductivity mechanism of CNT – polymer composites depends on direct conduction by the percolation phenomena along the CNTs interconnected network and the tunneling mechanism via an interface between the CNTs and the polymer matrix. In the present work we have functionalized MWCNT with –OH, –COOH and –S-O functional groups and then composites of above functionalized MWCNT were prepared with PMMA polymer. Conductivity measurements have been done on

these composite specimens and results are analyzed to conclude the effect of functionalization of MWCNT.

II. EXPERIMENTAL

Commercially available MWCNT were procured and used directly as starting material. Experimental details of functionalization with –OH, –COOH and –S-O functional groups are detailed.

The first type of MWCNTs are purified by HNO₃ acid and heat treated that get oxidized and the composites prepared using these as fillers have been labeled as o-CNT. The surface functional group of the OH-MWCNT is predominantly the hydroxyl –OH group the morphology and dimensions remain about the same as of as-synthesized and purified CNTs. The second type of MWCNTs are functionalized with carboxyl –COOH group (their composites labeled c-CNT) using acids H₂SO₄+HNO₃ replacing most of –OH of the pre-functionalized CNTs. This functionalization is led by defect sites on the sidewalls and the end caps. Hence, the length of COOH-MWCNT is considerably shortened compared to as purified ones. Both the –OH and –COOH functionalizations are covalent type where the π -electron structure of CNTs may get destroyed. Finally, the third type of MWCNTs (their composites labeled s-CNT) are functionalized with the polyelectrolyte (PAH)/TEOS with non-covalent bonding where the polyelectrolyte PAH wraps around the side walls of CNTs as described in earlier chapters 4/5. The TEOS coated on PAH, after hydrolysis forms the siloxane O-Si-O groups and replace some of the present –OH groups of the MWCNT.

The specimen of composites of notations o-MWCNT, c-MWCNT, s-MWCNT were prepared using differently functionalized MWCNTs with polymethylmethacrylate (PMMA) polymer were prepared. Fig 1 shows the SEM images of these three functionalized specimen.

The samples (200 μ m thick) cut in a strip form of dimensions 40mmX10mm (allowing electrode separation of 30mm) were placed onto an insulating board with tin solder islands to provide electrical connections for the Voltage source. A multimeter, a high resistivity meter Model 6517A, Keithley Instruments, Inc. is used that contains a set of picoammeter and voltage source. To create the connections directly onto sample's surface, in an easy, fast and reproducible way, the silver conductive paste was chosen [8], which does not require any particular equipment (such as metals sputtering or thermal evaporators devices) [9], just several minutes are required in order to let the solvent to evaporate. This way it also prevented any kind of warming of the composite samples which could have changed their properties. Prior to the measurements, the calibration and

resistivity capability was verified with the help of standard 2 MΩ (HW520, NTE Electronics, Inc.) and 20 MΩ (829620, RCA, Inc.) resistors measured values are all within the tolerance of 2 %.

Each sample was measured three times to have a statistical average value for the resistance and to see if the behavior observed was reproducible. For this purpose electrical connections between the voltage source and the fixture board were removed every time before each measurement. A low voltage range (± 10 V or ± 20 V, with a step of 0.1 V) was chosen for samples with wt.% of CNTs ≥ 1 mainly for two reasons: to avoid samples warming due to high current flow; and to maintain a threshold cut-off for currents higher than 1 A as prescribed for the multimeter. The Joule heating has been observed especially with samples with a CNTs load equal or higher than 4 wt.% and justifying this precaution. For this reason the range was moreover reduced between ± 7 V or smaller for some highly conductive samples.

Here, we analyze and discuss the influence of above functionalization schemes for MWCNTs on the conductivity of MWCNT-polymer composites particularly related to the dispersion/agglomeration of MWCNTs, the conductivity

percolation threshold and their conductive network forming ability.

III. RESULTS & DISCUSSION

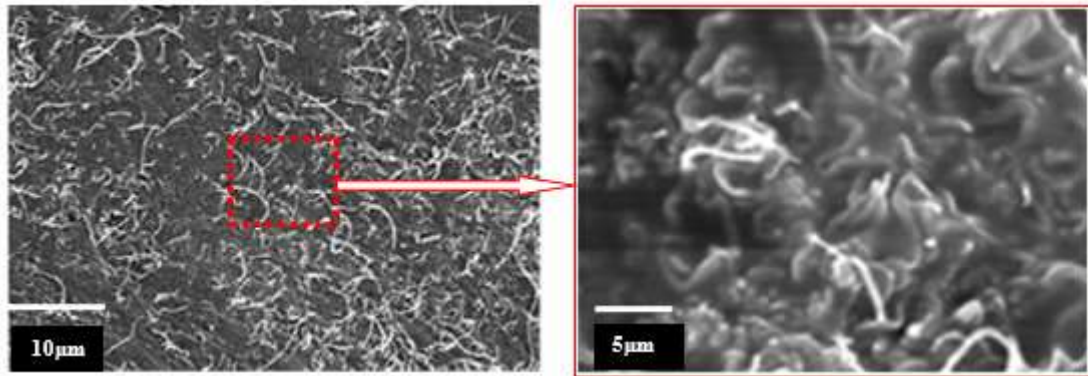
Here, we analyze and discuss the influence of above functionalization schemes for MWCNTs on the structure and conductivity of MWCNT-polymer composites particularly related to the dispersion/agglomeration of MWCNTs, the conductivity percolation threshold and their conductive network forming ability

Based on the SEM characterization result of the functionalized MWCNTs and their composites and results of the electrical DC conductivity behavior have been analyzed.

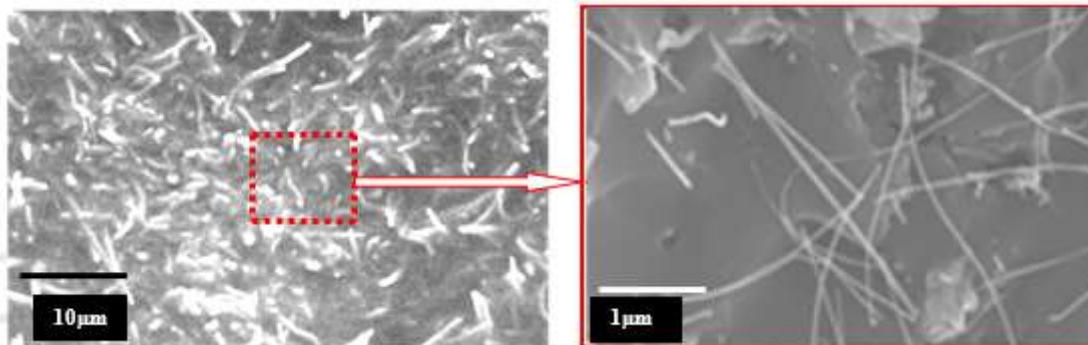
SEM images in fig 1(A) and fig 1(B) show the distinction between differently functionalized CNTs is not on the basis of functionalization alone; there are differences in their aspect ratios (Length/diameter) as well, though all of these using the same as- synthesized CNTs as noted in Table 1 also reproduced below for convenience in present discussions.

Property	CNT Type/Functionalization			
	Purified	OH	COOH	-Si-O
Type	MWCNT	MWCNT	MWCNT	MWCNT
Purity	85-90%	85-90%	85-90%	85-90%
Length	2-120 μ m	2-15 μ m	<5 μ m	2-15 μ m
Diameter	~60-90nm	~60-90nm	~60-90nm	~60-90nm
Curlyness	yes	yes	lesser	yes
Agglomeration	yes	No	no	Yes

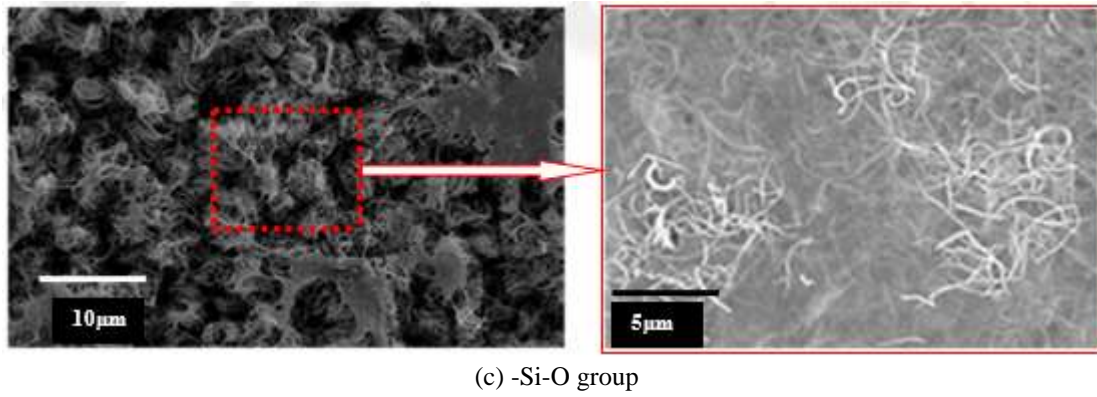
Table 1: Properties of functionalized MWCNT



(a) OH group

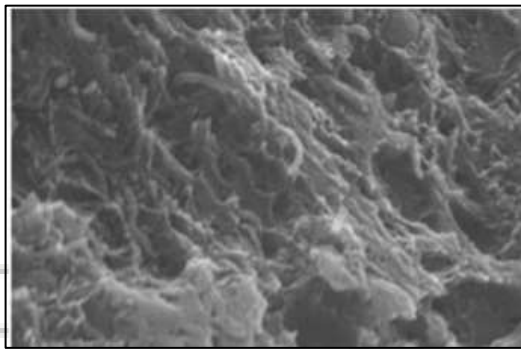


(b) COOH

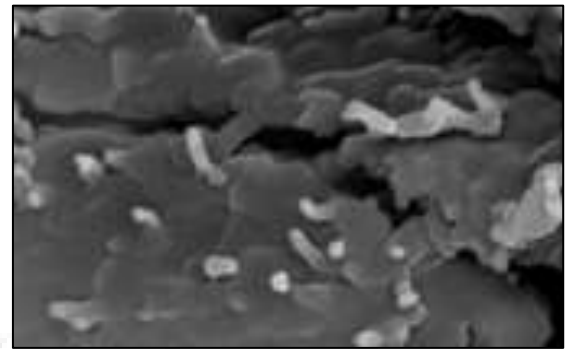


(c) -Si-O group

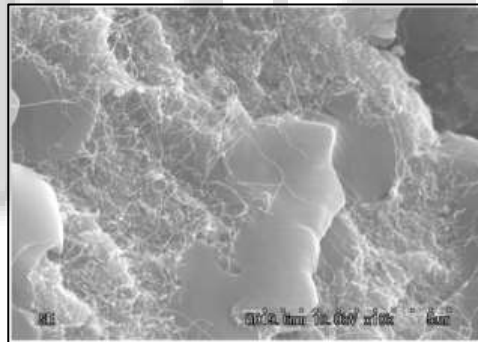
Fig. 1: (A) Scanning Electron Microscopy (SEM) images on surface of 2wt% functionalized MWCNT-PMMA polymer composite; MWCNT are functionalized by (a) OH group (b) COOH group (c) -Si-O group. Image panels on the right are magnified views for the region marked by red dashed area on the left panel image for the



(a)



(b)



(c)

Fig. 2: (B) SEM images on fractured surface of 2wt% functionalized MWCNT-PMMA polymer composite; MWCNT are functionalized by (a) o- MWCNT composite (b) c-MWCNT composite(c) s-MWCNT composite

Table 2 shows the resistivity of the composites of functionalized MWCNT with PMMA as a function of wt % of MWCNT. Fig 2 shows the percolation threshold for the three functionalized MWCNT-PMMA composites

Sl No.	MWCNT Concentration (wt%)	Resistivity (ρ), Ω .cm		
		Functionalization group		
		OH	COOH	-Si-O
1.	0.1	1.03×10^5	1.23×10^5	0.83×10^5
2.	0.3	1.13×10^5	1.33×10^5	0.71×10^5
3.	0.5	0.9093×10^4	-	0.125×10^4
4.	1.0	0.4545×10^4	3.58×10^3	0.166×10^3
5.	1.5	0.4343×10^4	-	0.833×10^2
6.	2.0	0.12×10^3	3.32×10^3	0.416×10^2
7.	2.5	0.869×10^2	-	0.238×10^2
8.	3.0	0.833×10^2	2.50×10^3	0.1923×10^2
9.	3.5	0.837×10^2	-	0.1653×10^2
10.	4.0	0.843×10^2	1.675×10^3	0.1586×10^2
11.	4.5	-	-	0.158×10^2
12.	5.0	0.813×10^2	3.08×10^2	0.1553×10^2

13	5.5	-	-	0.155×10^2
14	6.0	0.808×10^2	2.44×10^2	0.154×10^2
15	7.0	0.811×10^2	2.38×10^2	0.155×10^2
16	8.0	0.821×10^2	2.32×10^2	-
17	9.0	-	2.30×10^2	-
18	10.0	-	-	-

Table 2: Resistivity (ρ) of the functionalized MWCNT-PMMA polymer

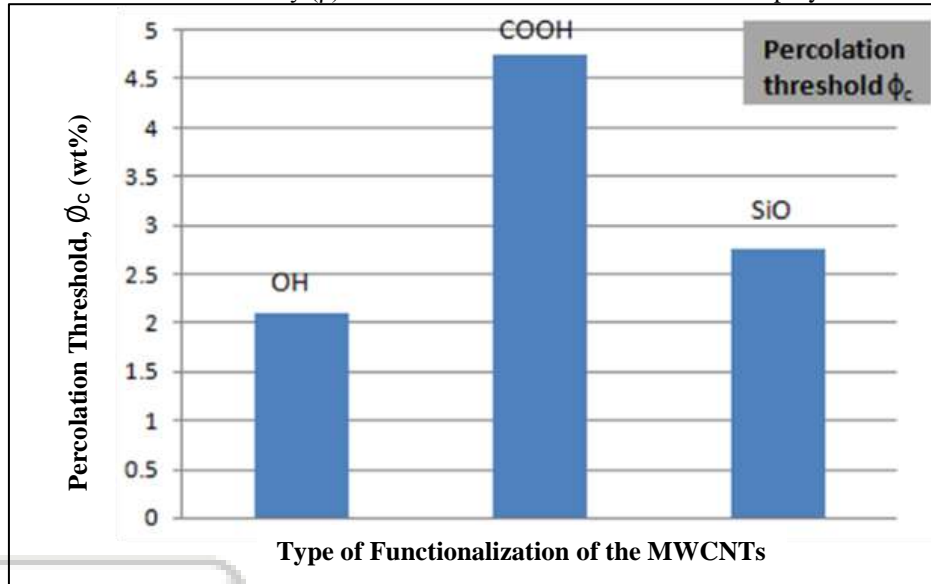


Fig. 3: Percolation threshold (ϕ_c) for the three functionalized MWCNT-PMMA composites

The ϕ_c is smallest ($\phi_c \approx 2.2$ wt%) for the case of OH-MWCNT fillers and largest for the COOH-MWCNT ($\phi_c \approx 4.6$ wt%) with intermediate value ($\phi_c \approx 2.75$ wt%) for the SiO-MWCNT as presented in charts in figure 2. Besides these differentiations, the width of percolation ($\Delta\phi_c$) also differ significantly. We define ($\Delta\phi_c$) as a range around which conductivity of the composite undergoes enhancements from that of the base polymer to the σ^u for the respective cases of functionalized CNTs. The conductivity rises sharply with smallest width $\Delta\phi_c$ as for the case of OH-MWCNT filler case whereas relatively more gradually and largest for SiO-MWCNT with intermediate value of slope for the case of COOH-MWCNT.

Two immediate conclusions can be drawn from the above observations for the conductivity and percolation threshold. First, that the non-covalent functionalization adopted for the MWCNT (by -Si-O group) by the PAH/TEOS scheme favors for achieving the enhancement in conductivity of the composites by about one order of magnitude compared to covalently bonded (OH and COOH groups) and in this respect expected to offer similar influence on conductivity for the respective composites which is not the case observed here hence indicating a differing conductivity mechanism for these two cases. On the other hand, the σ^u for COOH-MWCNT fillers have been observed to be lowest among the studied functionalizations. This is understandable since COOH-MWCNT possess much shorter length or are of smaller aspect ratios with larger inter-tube separation with larger tunneling resistivity and thus accordingly percolation threshold also is observed to be higher. The other conclusion from the above results is that the lowest percolation threshold does not ensure high value for the conductivity as observed for the case of composites with OH-MWCNT fillers. The

above observations and conclusions particularly one order of higher conductivity in composites for the case of non-covalently functionalized MWCNT fillers have significant relevance in explaining the comparative roles of functionalizations for ability to create the conductivity networks of CNTs in the insulating polymer, as to be discussed in the following. The conductivity and the percolation threshold of CNT/polymer composites depend on various other factors, such as the waviness and geometric structure of CNTs, the extent of dispersion of CNTs in the polymer matrices.

IV. CONCLUSIONS

It is concluded that physical structure of MWCNT changes with functionalization. The notion that well dispersed CNT fillers result to lower percolation and higher conductivity is not substantiated for the COOH functionalized filler MWCNTs. The COOH-MWCNTs are best dispersed among the three functionalizations studied in this work but of lowest conductivity and largest percolation threshold. A perfect dispersion state of CNTs leads to individual CNTs separated in the matrix, and therefore, a higher percolation threshold. Higher dispersion alone does not translate to higher conductivity.

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