Functionalized Multi-Walled Carbon Nanotube-Reinforced Epoxy-Composites: Electrical And Mechanical Characterization

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Abstract**—** *Carbon nanotubes (CNTs) got great attention because of their interesting physical and mechanical properties. Due to these interesting properties observed at the nanoscale have motivated scientific community to utilize CNTs as reinforcement in composite materials. In the present study, different CNTs and epoxy nano-composites with different wt% (1, 2, 3, and 4%) of f-MWCNTs were prepared and their surface morphology and orientation has been investigated in detail. Further, the surface investigation, electrical and mechanical tests were carried out on CNTs-filled and unfilled epoxy at maximum sonication time 30 minute to identify the loading effect on the properties of the materials. Experimental results depicts well dispersion of f-MWCNTs, significant improvement that the resistivity of pure epoxy decreased from 10^8 Ω.m to average value 10^3 Ω.m with 1, 2, 3, and 4wt% f-MWCNTs. The 4.5wt% CNTs/epoxy was attributed to poor dispersion of f-MWCNTs in the nanocomposte. The hardness of nanocomposite loading 1, 2, 3, 4wt% of CNTs, increased 20.7%, 23.02%, 25.62%, 29.09% respectively as compared to pure epoxy. We believe that our strategy for obtaining CNT–reinforced epoxy nanocomposites is a very promising technology and will open a new doors in fields of aviation, aerospace, marine and sporting goods.*

Keywords—Carbon nanotubes, epoxy, composite materials, surface morphology, electrical resistivity.

I. INTRODUCTION

Carbon nanotubes (CNTs), with their interesting electrical, mechanical and thermal properties combined with their dimensions have become important for many applications in nanotechnology such as nano-wires, transistors, field emitters, reinforced nano-composites and conducting filler in insulating materials. [1] Regarding extraordinary mechanical properties CNTs is used as filler to improve the mechanical properties of polymer composites. Furthermore, to strengthen various structural materials CNTs are used as additives in tiny portion e.g. baseball bats, golf clubs, or car parts [2-3]. It is considered as one of the strongest materials in universe having Young's modulus 270 - 950 GPa and tensile strength of 11 - 63 GPa. This strength is due to covalent bonds formed between the individual carbon atoms [4- 5]. In polymer composite materials covalent sp^2 bonds between carbon to carbon and hydrogen atoms is responsible for specific strength. Polymer composite have desirable properties to enhance the reinforce MWCNTs, however the mechanical properties of composite also depend on the quality of CNTs, dispersion, alignment and interfacial bonding between CNTs and the matrix. These composites have excellent properties in the field of aerospace application, electronics and automotive industries. Several reports have concluded the enhancement in mechanical properties of non functionalized CNT based polymer nanocomposites due to better surface interfaces but in some reports chemical functionalization have been utilized in order to improve the efficiency [6-8] Recently, more research interests explode towards the functionalized multi-walled Carbon Nanotubes on epoxy matrix composites due to their extensive potential applications in different fields e.g. electronics, aerospace automotive and sports industries. Zhou *et al.* [9] prepared CNTs epoxy composite material which is obtained using ultra sonication method, mechanical test results showed that modulus, tensile strength and fracture toughness properties enhance by different loading of CNTs as compare to pure epoxy, but in higher loading system the poor dispersions of CNTs in the composite. Maser *et al.* [10] studied the mechanical properties of CNTs epoxy composite material. The 0.1wt% CNTs results showed the young modulus and tensile strength is increases by 1.2% and 5.5% respectively compare to pure epoxy. Husaen *et al.* [11]

has prepared the CNTs epoxy composite material having CNTs different loading weight percentages and found that the flexural and tensile modulus was improved as compare to pure epoxy. Wong *et al.* [12] also studied that there was a significant improvement in young's modulus, hardness and tensile strength of CNTs functionalize and non- functionalize composite material. In the present study, we demonstrated successfully the dispersions of functionalized MWCNTs in epoxy resin with different wt% and sonication time using a microfluidic processor and their effect on the structural, mechanical and electrical properties. Analysis and microstructure provide new insight occur during process.

II. EXPERIMENT

2.1. Method and Material:

The materials used in this study were of analytical grade. Functionalized Multiwall carbon nanotubes with NH_2 content (f-MWCNTs) purity ~ 95%, were obtained from Chengdu organic Chemicals Co. Ltd Chinese Academy of Sciences. Epoxy resin (5052) and Hardener (dicyandiamide) was provided by National Center for Physics (NCP) Islamabad, Pakistan.

In the present work the f-MWCNTs/epoxy nanocomposites were prepared by solution mixing method. These epoxy composites were prepared by taking loading of f-MWCNTs 1,2,3,4 and 4.5wt% in the epoxy resin. The f-MWCNTs were first dispersed in ethanol solution and placed on sonication only for 10 minute, after complete evaporation of ethanol the f- MWCNTs was added to the known amount 15g epoxy resin and sonicated for 10 minute at temperature 69°C.After sonication 5.0g mixture of f-MWCNTs/epoxy added to 1.9g hardener, then mixed through glass rod in a beaker and placed in a column which is our first require sample. The rest of 10.0g mixture of f-MWCNTs/epoxy is again placed on sonication for 10 minute heated at temperature 69°C, again 5.0g mixture of f-MWCNTs/epoxy added to hardener which is our second require sample having the same percentage of f-MCNTs but only the sonication time was changed. The same process was practice for the rest of 5.0g mixture which is our next sample. Using the above procedure we have prepared different composite samples containing f-MCNTs 1,2,3,4 and 4.5wt% to epoxy respectively. Keeping the temperature at 69°C for all the samples with different sonication time. All composite samples were cured for 4hour at 100°C in a furnace.

2.2 Characterizations:

As-prepared samples were characterized using different analytical techniques and instruments. To observe the related morphologies the samples of the f-MWCNTs-epoxy nanocomposites were characterized by scanning electron microscopy (SEM, HITACHI S-3400 N). Raman spectroscopy was carried out using an apparatus (Model Lab RAM HR Company He-Ne laser wavelength 632.8nm). In order to see the vibrational, rotational frequency modes in composite, raman spectroscopy was employed to analyze the active band regions. High voltage trigger machine to measure the electrical conductivity was carried out at National Centre for physics (NCP) Islamabad. Shimadzu micro hardness (hmv) tester was use in order to analyze the mechanical properties of as-prepared different composites. The initial applied load was 490.3mN during 10 seconds.

III. RESULT AND DISCUSSION

3.1. Morphology Characterization

The surface morphology of the as-prepared samples was investigated by scanning electron microscopy (SEM). **Fig. 1 (a)** presents smooth fracture surfaces of pure epoxy resin as compare to f-MWCNTs-epoxy nanocomposites. **Fig. 1(b-e)** showed the morphologies of different wt% f-MWCNTs-epoxy nanocomposites. As can be seen clearly from **Fig. 1(b),** epoxy containing 1wt% CNTs shows uniform dispersion of carbon nanotubes, these type of explanation have found in previous work. [13] A small number of rod like CNTs can be seen due to their small wt% of f-MWCNTs. Similarly the epoxy composite containing 2 wt% CNTs shows the growth of carbon nanotubes are randomly oriented with clear tube structure having low agglomeration **(Fig. 1c). Fig 1 (d-e)** containing 3wt% CNTs and showed that there is not clear structure of CNTs due to low magnification scale which gives evidence for improved intrfacial interaction between CNTs and epoxy matrix. It gives CNT structure with clear length and diameter. SEM images also showed the surface of nanocomposite become rougher as compare with the pure epoxy. **Fig 2a-c** shows nanocomposite containing 4wt% f-MWCNTs and shows just growth of carbon nanotubes. High agglomeration and low uniform dispersion due to high load of 4.5wt% of f-MWCTNs which are also supported by literature [14]. The SEM results evident that as the CNTs content increases up to 4wt% of f-MWCTNs, increases the surface roughness and shows the clear structure of carbon nanotubes. It is also gives evidence for improved intrfacial interaction between CNTs and epoxy matrix which is also agreement with the previous work[15].

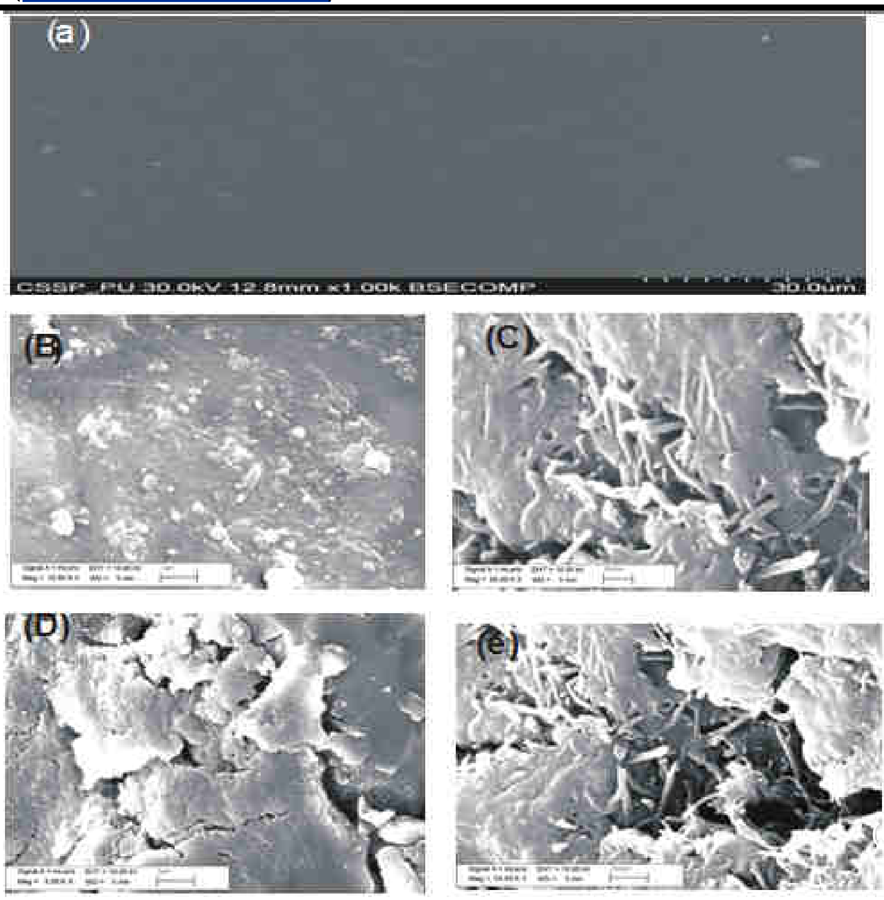

Fig.1: SEM images (a) shows pure epoxy surfaces; (b-e) shows 1, 2 and 3 wt% f-MWCNTS/epoxy composite surfaces.

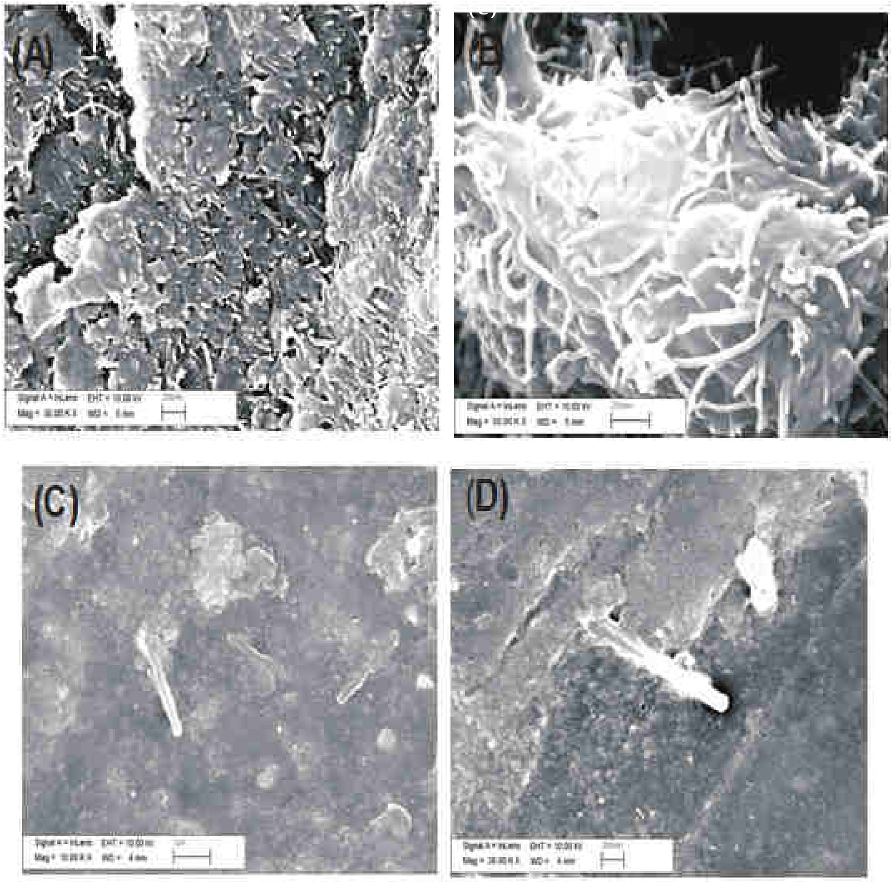

Fig.2: SEM images (a-b) shows 4 wt% f-MWCNTS/epoxy composite surfaces; (c-d) shows 4.5 wt% f-MWCNTS/epoxy composite surfaces.

Furthermore the raman spectrum have been used to confirm the material. **Fig. 3 (a**) showed that the raman spectrum of pure epoxy having only one peak which lies round about 1430cm^{-1}, similarly **Fig (3b-f)** showed there are two main peaks D band and G band respectively. Mostly the D band lies between 1300–1400 cm^{-1} and G band which are located near 1600 cm^{-1} [16]. In the following images the D and G band lies at1330 cm^{-1} and 1600 cm^{-1} respectively. The peak which lies at 1430 cm^{-1} is due to epoxy. The D band is due to the defects with the CNTs, it is also refers as disorder band, defects band and its intensity is relative to G band. The G band can be used to determine the orientation of the carbon nanotubes in a composite which assigned the vibration of C-C bond also gives the information about graphitic characteristic occurs at around 1600 cm^{-1} [17-19] (**Fig. 3**).

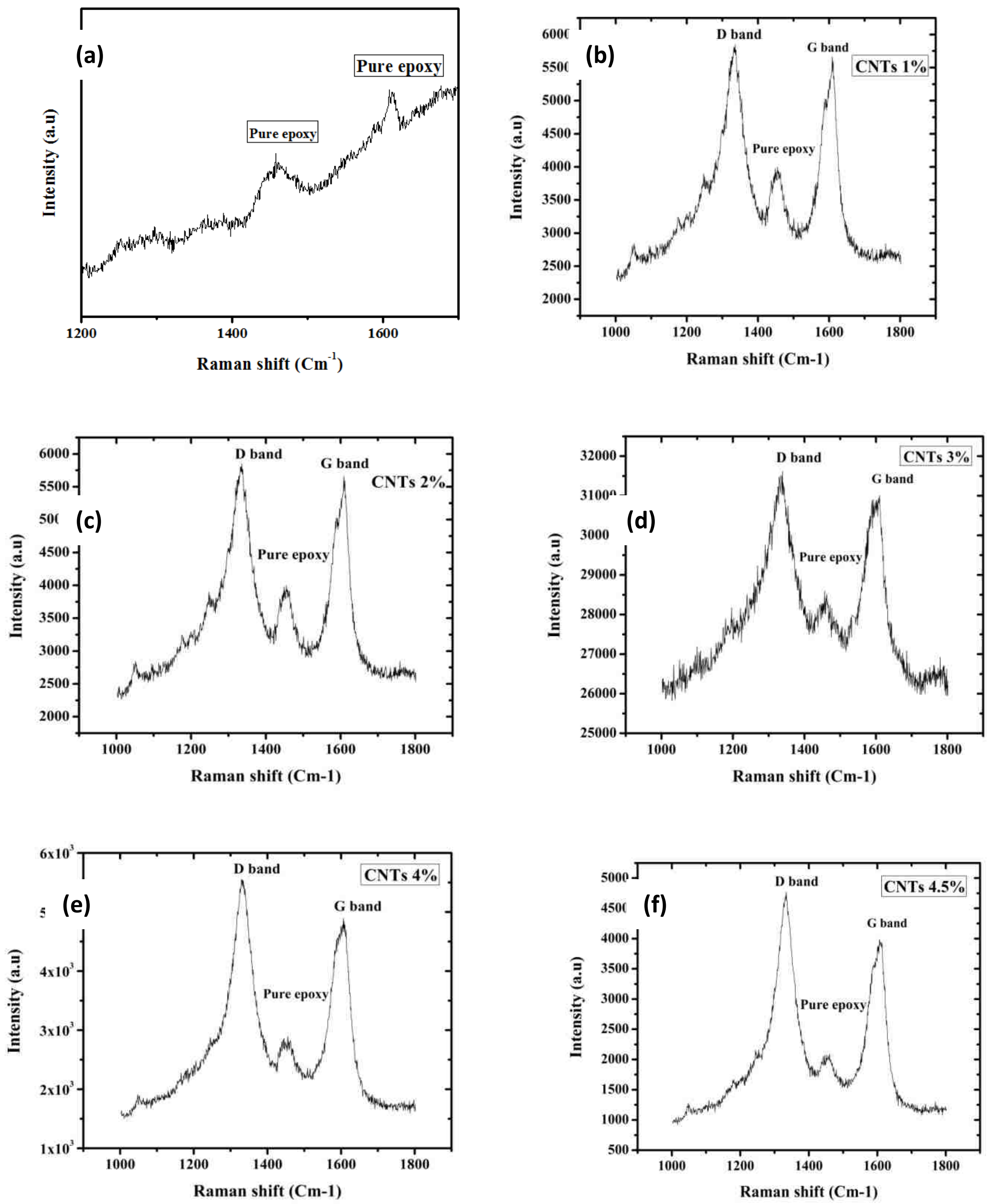

Fig.3: Raman Spectrum of (a) pure epoxy; (b-f) f- MWNTs/epoxy composite in the range of 1000–1800 cm^{-1} .

3.2. Electrical properties of nanocomposite:

The electrical properties of neat epoxy and MWCNTs/ epoxy based composite material were measured by using multi-channel High Voltage Trigger machine at National centre for physics (NCP) Islamabad. The samples were cut into square shape with area 1 cm^{-1} having different thickness. The copper tap was used as electrodes. Epoxy resin is generally an insulator. The electrical resistivity of epoxy (5052) was measured 4.21×10^{8} Ω.m. The resistivity of the composite was calculated from the geometry and measured impedance of the sample [20]. Different percentages of CNTs were loading into epoxy matrix, showing the resistivity results of the samples **(Fig. 4)**. In fig. 4 the zero percent CNTs shows the resistivity of pure epoxy. These results shows some considerable change occurs in the resistivity of nanocomposite as compare to the resistivity of pure epoxy. The average value of resistivity drops by order 10^4 and10^3Ω.m sample having 1, 2 wt% and 3, 4wt% of f-MWCNTs respectively. This extraordinary change is due to the maximum sonication time 30 minute compared to 10 and 20 minute which causes the well dispersion of CNTs in the epoxy matrix [21]. The samples containing 4.5wt% of CNTs there was a minute change in the resistivity because of poor dispersion and high agglomeration there is no path for electron mobility, due to high concentration of CNTs.

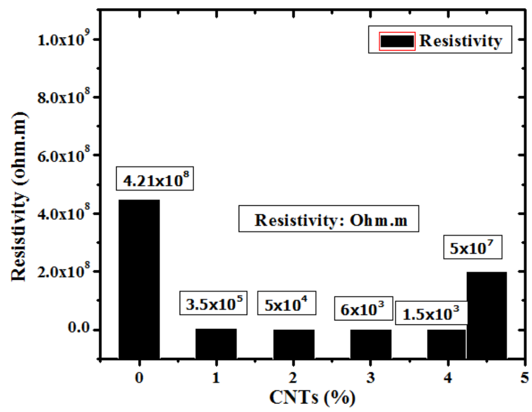

Fig.4: Resistivity verses CNTs wt% sonication time 30 minute at temperature 69ºC.

3.3. Mechanical properties of nanocomposite:

The micro hardness testing machine (Shimadzu hmv micro hardness tester) was used to measure the hardness of CNT composite material. On each f-MWCNTs/epoxy nano composite sample, three points were measured in order to get the average reading. This average value was recorded as the hardness value. In this test the load was used 490.3mN and load duration is 10sec.In the following table 1.1 the hardness values of different composite were showed [11]. The table 1. Showed the hardness increased to about 20.7%, 23.02% and 25.61%, 29.09% for sample with 1, 2, 3 and 4wt% CNTs respectively. The reason for increased hardness values due to an overlap and stacking which reduce the movement of polymers molecules which lead to increase the resistance of the material to cut and scratch. Composite having 4.5wt% f-MWCNTs, the hardness decrease may be due to the existence of a poor bonding interface between the nanotubes and the matrix. High agglomeration and low uniform dispersion due to high load of 4.5wt% of f-MWCTNs is also confirm from SEM images as shown in fig 2. This table has completely explained by graph Vickers hardness Vs CNTs percentage as shown in fig 5.

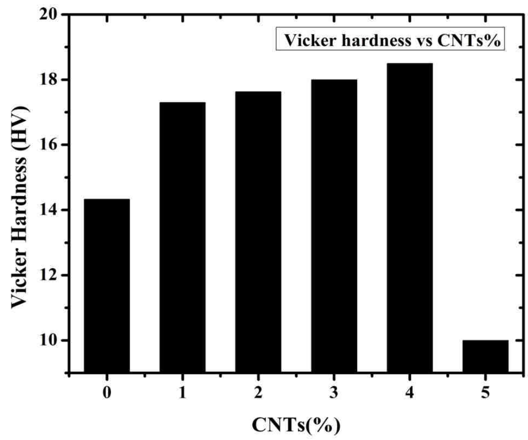

Fig.5: Vickers hardness Vs CNTs wt%.

Table.1: Hardness of epoxy and f-MWCNTs/epoxy

Epoxy+CNTs%	**Vicker hardness (Hv)**	**Improvement when comparing with epoxy.**
Epoxy	14.33	N/A
CNTs 1%	17.30	20.7%
2%	17.63	23.02%
3%	18.0	25.61%
4%	18.50	29.09%
4.5%	9.87	N/A

IV. CONCLUSIONS

In the present study, different types of CNTs and epoxy nanocomposite have been prepared and were tested for their electrical and mechanical properties. The investigation of CNTs epoxy nanocomposite gives evidence for improved interfacial interaction between nanotubes and epoxy matrix. It is observed that the surface roughness increased which absorb more energy which had better strength and toughness. The electrical resistivity of pure epoxy was measured $4.21x10^8$ ohm.m decreased by order of 10^3 Ω.m. This extraordinary change is due to the maximum sonication time 30 minute compared to 10 and 20 minute except sample having 4.5wt% of f-MWCNTs. It is also investigated that the increased the sonication time with increasing CNTs wt% up to 4wt% decreased the resistivity due to uniform dispersion of CNTs in epoxy matrix. This green and low budget method and materials invite future investigations on the design of new composites which will have more interesting applications such as aviation, aerospace, marine and sporting goods.

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