Synthesis of multi-walled carbon nanotubes and their application in resin based nanocomposites

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Abstract. Multi-walled carbon nanotubes (MWCNTs) were synthesized by catalytic decomposition of hydrocarbon gas using chemical vapor deposition method. Synthesis was done at different growth temperatures and catalyst ratios. These MWCNTs were dispersed in epoxy resin (E-51) and the ir effect on mechanical strength of epoxy nanocomposites was studied. Increase in the mechanical strength of epoxy was observed with the addition of CNTs. The surface characterization was done by using optical microscope and scanning electron microscope (SEM). Mechanical properties were determined by the general tensile strength testing method.

1. Introduction

Carbon nanotubes (CNTs) are hollow nanometer size tubes of graphitic carbon. A carbon nanotube can be imagined as a graphene sheet rolled in the form of a seamless cylinder. The synthesis of CNTs can be back tracked to 1952 when Radushkevich et al. [1], a Russian group, published the first transmission electron microscopy (TEM) image supporting the tubular nature of the nanometric-sized carbon filaments. Iijima [2], from the NEC Laboratory in Tsukuba, Japan, was the first to identify the carbon nanotubes structure using High-Resolution Transmission Electron Microscopy (HRTEM). Afterwards, the field of carbon nanotubes was launched seriously. CNTs have exceptional mechanical [3-5], electrical [6-8] and thermal properties [9-11]. Their superior properties make them the most promising nanomaterials in the 21st century for a wide range of applications.

CNTs can mainly be divided into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). A single-walled carbon nanotube can be considered as a single graphene sheet rolled into a tube, whereas, the multi-walled nanotubes can be described as a number of concentric SWCNTs having different diameters. The synthesis of CNTs can be done by various methods: arc-discharge [12], laser ablation [13], and chemical vapor deposition [14]. Chemical vapor deposition (CVD) is relatively a simple and economical technique for the synthesis of CNTs as compared to arc-discharge, and laser ablation methods. It can be done at low temperature and ambient pressure. This method offers higher purity, larger yield, and better control on the growth parameters and structure. To date, CVD is considered as a cost-effective method for the production of good quality CNTs. It has a potential to scale up the production of CNTs to the commercial level [15-18].

The most intriguing applications of CNTs are in CNTs based polymer nanocomposites. The effective utilization of CNTs in composites strongly depends upon their homogeneous dispersion in the host matrix, and an efficient load transfer to the CNTs [19-20]. Hence, good dispersion of CNTs is
a fundamental feature to maximize their effect. In this paper, we report the synthesis of MWCNTs by catalytic decomposition of hydrocarbon gas (C\(_2\)H\(_2\)) using CVD method. The synthesis conditions were optimized in terms of growth temperature and catalyst ratio. These CNTs were heat treated for purification, and the purified CNTs were used for further studies. A low content of MWCNTs (~ 0.2 wt\%) was used for these studies. The purified CNTs were dispersed in ethanol by ultrasonication for uniform dispersion in epoxy resin (E-51). A protocol was devised for homogeneous dispersion of MWCNTs in epoxy resin, and the CNTs based epoxy nanocomposites were prepared by following this protocol. The purpose of this study is to synthesize CNTs and to study their effect on mechanical strength of epoxy nanocomposites.

2. Experimental

2.1. Materials
The MWCNTs used in this study were synthesized at NCP, Islamabad. The synthesis was done by chemical vapor deposition method. Epoxy polymer matrix was prepared by mixing epoxy resin E-51, hardener (70-acid anhydride), and accelerator (N, N-dimethylbenzyl amine). Their chemical formulae are shown in figure 1. The precursors (Chromium acetate, Nickel Nitrate, Iron Oxide, conc. HCl, and Ethanol), carrier gas N\(_2\), and source gas C\(_2\)H\(_2\) used in this study were of high purity.

![Figure 1: Epoxy resin, hardener, and accelerator used in this study.](image)

2.2. CNTs synthesis
The synthesis of CNTs was done by catalytic decomposition of C\(_2\)H\(_2\) using CVD method. A number of experiments were performed to optimize the experimental conditions like gas flow rate, reaction time, pre and post reaction temperature, reaction temperature, and mixing ratio of hydrocarbon gas and inert gas. A constant flow rate of nitrogen gas was maintained during heating. The schematic diagram of CVD setup is shown in the figure 2.
A combination of Fe, Ni, and Cr was used as catalyst for the synthesis of CNTs. Liquid phase impregnation method was employed for catalyst preparation. Optimized amount of Chromium acetate, Nickel Nitrate, and Iron Oxide was dissolved in conc. HCl, and heating was done at 70°C for one hour. The catalyst substrate was placed at the center of horizontal quartz tube in the tube furnace. The furnace temperature was maintained at 850°C for half an hour in the N₂ flow to activate the catalyst. The synthesis was done at different growth temperatures (600-750°C), keeping the ratio of C₂H₂ : N₂ at 1:10 sccm. After the completion of reaction, the flow of C₂H₂ was stopped and the reaction temperature was maintained in the reactor for an hour in flowing nitrogen. Then the reactor was cooled down to the room temperature under the same flow rate of N₂.

2.3. Growth mechanism of carbon nanotubes
The growth mechanism of carbon nanotubes by catalytic decomposition of hydrocarbon gas can be described as follows. Hydrocarbon gas decomposes into carbon and hydrogen when it comes in contact with the high temperature catalyst metal particles. The decomposed carbon dissolves in the metal particles and reaches a supersaturated state. At this stage the dissolved carbon precipitates out and acquires an energetically stable state, by crystallizing in the form of seamless cylinders of carbon nanotubes. Depending upon the catalyst-substrate interactions, CNTs can grow by two different growth mechanisms in a CVD process. The first mechanism is called tip-growth mechanism and the second method is called base-growth mechanism. In the first method, the catalyst-substrate interactions are weak and the metal particle is pulled up at the top of grown CNTs. In the second method, the catalyst-substrate interactions are strong and the CNTs grow on the metal particle. The both growth mechanisms of CNTs are shown in figure 3.
2.4. Preparation of nanocomposites

The protocol for preparation of CNTs dispersed epoxy nanocomposites is shown in the following flow chart figure 4.

The synthesized MWCNTs were heat treated at 400°C for 1 hr in ambient atmosphere for purification. Ethanol was added to the purified CNTs and sonication was done for 2 hrs for debundling of agglomerated CNTs. The epoxy resin was added and the mixture was further sonicated for 2 hrs. After sonication, the solvent removal was done. This was done by mechanical mixing of the mixture under evacuation in a chamber. To ensure that the solvent is completely removed, the mixture was weighed before the addition of ethanol and after its removal. The hardener was added and sonication was done for 1 hr, followed by 1 hr mechanical mixing and evacuation. Finally, accelerator was added and mechanical mixing and evacuation was done for 30 minutes. The uniform dispersion
of CNTs in epoxy was checked by an optical microscope. The CNTs dispersed epoxy was poured in a mold for making tensile strength testing samples, and was cured in an oven. Neat epoxy resin samples were also prepared for the comparison of results. The cured dog bone shaped tensile strength testing samples of neat epoxy (orange) and CNTs doped epoxy (black) are shown in figure 5.

![Figure 5. Tensile strength testing samples: Neat epoxy (orange) and CNTs doped epoxy (black) samples.](image)

### 3. Result and Discussion

#### 3.1. Synthesis

Parametric study was done for optimization of different parameters of the fixed-bed reactor. Catalyst composition, flow rates of nitrogen and acetylene gas, flow time of carbon source, growth temperature, and retention time were optimized. Synthesis temperature is the most important factor in our studies. C$_2$H$_2$ undergoes pyrolysis above 700°C [21]. The end products of C$_2$H$_2$ pyrolysis are polycyclic aromatic hydrocarbons (PAHs), which are thermodynamically stable [22]. These byproducts deplete the relative concentration of the CNTs carbon source. Also they can grow large enough to deactivate the catalyst by blocking active sites. These considerations restrict the large C$_2$H$_2$ concentration used for synthesis for the limited time period.

The SEM images of the systematic growth of CNTs at different reaction temperatures are shown in figure 6. At 600°C no growth of CNTs was observed (fig.6. a-1, a-2). As can be seen in the figure, uniform circular particles of carbon are grown instead of CNTs. These circular particles have diameter averaging around 100 nm. On increasing the growth temperature to 700°C, the growth of the CNTs is evidenced along with circular carbon particles (fig.6. b-1, b-2). These particles are larger than those observed at the previous growth temperature, but still they maintain the circular shape. More than half of the sample contains these particles. Further increase in growth temperature (750°C) results in better growth of CNTs (fig.6. c-1, c-2). Two type of CNTs are grown; one in the range of 150-100 nm and the other less than 100 nm. Still a significant part of the sample contains amorphous carbon. The Cr content was doubled keeping the amount of Ni and Fe same for the substrate preparation, and the experiment was repeated under the identical conditions. It can be evidenced in the figure 6 (d-1, d-2) that most of the CNTs grown in this case are less than 100 nm, only a few CNTs lie in the range of 150-100 nm. Also these CNTs are clean as compared to those grown in the previous cases and almost no amorphous carbon is observed in this case.
3.2. CNTs dispersed epoxy nanocomposites
Dispersion of synthesized CNTs in epoxy resin was done following the flow chart discussed in section 2.4 (figure 3). The dispersion of CNTs in epoxy was checked visually and by an optical microscope. A comparison of dispersion is shown in figure 7.

The optical micrographs of homogeneous and non-homogeneous dispersion of CNTs are shown in the figure 7 (a, b). Agglomerates of CNTs can be seen in figure 7 (a). In this case CNTs were directly dispersed in the epoxy resin by mechanical mixing. No solvent was used for dispersion. After 4 hrs of mechanical mixing the mixture was poured in the mold and curing was done. After mixing, no
agglomerates were observed on visual inspection. A drop of this mixture was placed on a glass slide and after a few hours it was showing two shades. When the slide was checked under a microscope the clustering of CNTs was apparent. On curing CNTs agglomerates were observed at the bottom of the cured film, as shown in the figure 7 (c). This shows that by mechanical mixing CNTs were not completely dispersed in the epoxy. Only partial dispersion was achieved and the van der Waal forces were strong enough to make the agglomerates of CNTs after mechanical mixing. On the other hand, when the dispersion was done using a solvent, following the protocol discussed in section 2.4, the dispersion was homogeneous and no agglomeration was observed in cured and uncured samples. This is shown in figure 7 (b, d). This effect was further confirmed when the tensile strength samples were prepared and tested.

To measure the effect of CNTs on the strength of epoxy samples with specific size were prepared, as shown in figure 5. Tensile testing (ASTM D 638) was done by Instron tensile tester at a cross speed of 2mm/min at 25°C. A batch of five samples was tested and the average value was reported.

Three types of samples were prepared:
1. Direct mixing of CNTs in epoxy without solvent
2. Mixing of CNTs following the protocol discussed in section 2.4
3. Neat samples of epoxy without CNTs (for comparison)

The CNTs doped epoxy samples (~ 0.2 wt%) show greater strength (84 MPa) as compared to the pure epoxy samples (72 MPa). On the other hand, the samples prepared by direct mixing of CNTs showed a decrease in the strength and their value (45 MPa) was even less than the neat epoxy samples. This improvement in UTS can be attributed to the high specific mechanical properties and high aspect ratio of the CNTs, when it is homogeneously dispersed in the epoxy matrix. This shows that addition of carbon nanotubes enhances the stress transfer effect of epoxy on application of a load, resulting in overall enhancement in the strength and plasticity of the resin matrix. The same, even better, effect has been observed in the strength of carbon fiber based epoxy composites on addition of CNTs (results not shown here). On the contrary, agglomerates of CNTs act as impurity sites in the epoxy which result in reduction in the strength.

This confirms that the effective utilization of CNTs in composites strongly depends upon their homogeneous dispersion in the host matrix. If a homogeneous dispersion may lead to enhancement in the properties, then a poor dispersion of CNTs may destroy the existing properties. Hence purification of CNTs and their good dispersion in epoxy resin play a key role to maximize the effect of CNTs on the overall properties of epoxy based composite system.

4. Conclusions
Carbon nanotubes having diameter in the range of 50 - 150 nm and less were successfully synthesized by the catalytic chemical vapor deposition of acetylene gas over Ni–Cr–Fe. It has been observed that certain parameters like growth temperature, catalyst composition, and flow time of acetylene have strong influence on the synthesis of carbon nanotubes. The affect of addition of these CNTs on mechanical properties of epoxy nanocomposites was also studied. When the CNTs are homogeneously dispersed, a small addition of CNTs (~ 0.2 wt%) may increase the strength of epoxy resin. This On the other hand, a poor dispersion of the same amount of CNTs may decrease the existing properties. The comparison of these result shows that improvement in the strength of epoxy resin with doping of CNTs strongly depends upon better dispersion CNTs in epoxy resin.

5. References
[1] Radushkevich L V and Lukyanovich V M 1952 Zurn. Fisic. Chim. 26 88
[2] Iijima S 1991 Nature. 354 56
[3] Poncharal P, Wang Z L, Ugarte D, and Heer W A 1999 Science 283 1513
[4] Tracy M M J, Ebbesen T W and Gibson J M 1996 Nature.381 678
[5] Wong E W, Sheehan P E and Lieber C N 1997 Science. 277 1971
[6] Zhu H W, Xu L, Wu D, Wei B Q, R Vajtai and Ajayan P M 2002 Science. 296 884
[7] Li Y, Kinloch I A and Windle A H 2004 Science. 304 276
[8] Zhou W, Vavro J, Guthy C, Winey K I, Fisher J E and Smalley R E 2004 J. Appl. Phys. 95 649
[9] Yosida Y 2000 J. Appl. Phys. 8 3338
[10] Berber S, Kwon Y K and Tomańek D 2000 Phys. Rev. Lett. 84 4613
[11] Foygel M, Morris RD, Anez D, French S and Sobolev V L 2005 Phys. Rev. B 71 104201
[12] Journet C, Maser W, Bernier P, Loiseau A, Lamy D, Chapelle M, Lefrant S, Deniard P, Lee R and Fischer J 1997 Nature. 388 756
[13] A Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, Xu C, Lee Y H, Kim S G, Rinzler A G, Colbert D T, Scuseria G E, TomoN, Fischer J E and Smalley R E 1996 Science. 273 483
[14] S Bethune D S, Klang C H, de Vries M S, Gorman G, Savoy R, Vazquez J and Beyers R 1993 Nature. 363 605
[15] Govindaraj A and Rao C N R 2002 Pure. Appl. Chem. 74 1557
[16] Rao C N R and Govindaraj A 2001 Proc. Indian Acad. Sci. (Chem. Sci.) 113 375
[17] Fonseca A, Hernadi K, Piedigrosso P, Colomer J F, Mukhopadhyay K, Doome R, Lazarescu S, Biro L P, Lambin Ph, Thiry P A, Bernaerts D and Nagy J B 1998 Appl. Phys. A 67 11
[18] Lee C J, Lyu S C, Kim H W, Park C Y and Yang C W 2002 Chem. Phys. Lett. 359 109
[19] Gojny F H, Nastalczyk J, Roslaniec Z and Schulte K 2003 Chem. Phys. Lett. 370 820
[20] Villoria R G, Miravete A, Guarero J, Chiminelli A and Tolosana N 2006 Composites Part B: Eng. 37 273
[21] Cui H, Zhou O and Stoner B R J. Appl. Phys. 88 6072
[22] Okai M, Muneyoshi T, Yaguchi T and Sasaki S 2000 Appl. Phys. Lett. 77 3468