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# Studies on structural defects on $^{60}Co$ irradiated multi walled carbon nanotubes.

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**Abstract**

An attempt is made to study the effects of gamma irradiation on multi walled carbon nanotubes (MWCNTs) with a specific focus on surface modification, structural changes and identification of irradiation generated defects on their surface. The as-received MWCNTs were chemically treated in order to attach required functional group on the surface and to remove traces of metallic impurities. The MWCNTs were then gamma irradiated at 25, 50, 75 and 100 kGy doses. Micro Raman analysis was performed on irradiated MWCNTs to estimate the irradiation induced defects on their surface, which revealed that the number of defects increased with dose. XRD analysis was also performed to observe the same and it was revealed that the MWCNTs were subjected to micro-straining. The selective area electron diffraction pattern revealed that traces of amorphous carbon were formed after irradiation. Various defects such as bending, variation of internal and external diameter, wall damages formed on the MWCNTs was verified using TEM. It is concluded that subjecting MWCNTs to irradiation sources has produced structural changes and defects on their surface which can influence the properties of nanocomposites.

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*Keywords:*

## 1. Introduction

Not too late after carbon nanotubes (CNTs) have been discovered, it was realized experimentally that the as grown CNTs contain a number of defects and impurities. In reality, CNTs are rarely perfect, it was reported by Iijima et al. (1992) that the CNTs had a number of defects and impurities, which result during manufracturing, processing and

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also during irradiation processess. Krasheninnikov et al. (2004) reported that the number of defects increased with energy of irradiation and there is a possiblity of formation of different defects like point defects e.g. vacancy and interstitial defects, strains, adatoms, pentagon-heptagon pairs, pentagon-octagon-pentagon pairs etc. It is noted that the defects in CNTs were created during irradiation only if the incident particle was energetic enough to displace Carbon atoms, and the minimum incident electron energy required to remove a Carbon atom by a knock-on collision was found to be 86 keV, Koutsky et al. (1994), and Smith et al. (2001). Studies of Hu et al. (2003) revealed that the defects formed on CNTs due to irradiation are expected to increase the CNT-polymer adhesion and improve its mechanical properties. Charlier (2002) reported that the irradiation of CNTs extracted atoms from their honeycomb lattice continuously or at random, which caused the formation of vacancies on their surface. These vacancies would further cluster and forms into large holes in the structure resulting the formation of a three-coordinate, highly defective carbon network. It was also reported that the irradiation not only produced the defects but also formed covalent bonds between the tubes of CNTs.

These defective sites of CNTs are more reactive than the perfect nanotubes due to their high electron affinities, Zhou et al. (2003). Watts et al. (2003) reported that CNTs acted as polymer antioxidants due to their high electron affinity. Studies of Zeynalov et al. (2008), proved that the defects formed on the CNTs lead to antioxidant capability of CNTs. Schultz et al. (2009) reported that CNTs are extremely effective antioxidants and their oxygen-radical scavenging activity was reported to be about 40 times greater than that of radio-protective dendritic fullerene. It was indicated by Galano [2010] that the antioxidant activity of functionalized CNTs were increased significantely compared to that of un-functionalized CNTs. Ritter et al. (2006) concluded that the number of defects in the CNTs increased with irradiation dose leading to accumulation of vacancies causing weakening of the inter carbon bonds. Recent studies on gamma irradiated MWCNTs and their composites have shown that they exhibited antioxidant characteristics due to their high electron affinities and thus they acted as radical scavengers in polymers, Morlanes et al. (2012) and Sreekanth et al. (2012, 2013).

Although a huge amount of theoretical work has been carried out to understand the origin of various kinds of structural defects in CNTs, very little is known experimentally. A better understanding on the mechanism of enhancement of properties of the MWCNTs reinforced composites is possible if the nature and behavior of the defects are studied systematically. Thus, the present study is aimed to focus on the influence of gamma irradiation on the structure, identification of defects formed on MWCNTs subjected to different doses of irradiation.

## 2. Materials and methods

### *2.1 Multi walled carbon nanotubes (MWCNTs)*

The MWCNTs were purchased from M/s Shenzhen Nanotech Port Co., Ltd., China. The manufacturers' specifications of MWCNTs are as follows: outer diameter 40-60 nm, length 5- 20 µm, purity - 95 wt. %, ash content < 1.5 %, density – 2.16 g/cc, special surface area > 200 $m^2/g$. Chemical treatment of the MWCNTs was performed as suggested by Esumi et al. (1996).

### *2.2 Gamma irradiation*

The chemically functionalized MWCNTs were then gamma irradiated in air by $^{60}Co$ source at a dosage rate of 2.5 kGy/h upto 25, 50, 75 and 100 kGy cumulative irradiation dose. The irradiation was performed at M/s Microtrol Sterilization Private Limited, Bangalore, India.

### *2.3 Fourier transform infrared spectroscope (FTIR)*

A Thermo fisher IS10 FTIR spectrometer was used to obtain the spectrum of the samples. The MWCNTs sample before and after irradiation was obtained using in the wave number range of 400 – 4000 $cm^{-1}$.

### 2.4 Transmission electron microscope (TEM)

A 200 kV Transmission Electron Microscope, JEOL JEM 2100, was used to identify the defects formed on the surface of MWCNTs after the irradiation process. High resolution TEM and selective area electron diffraction (SAED) were also used to obtain the crystal planes of MWCNTs.

### 2.5 X-ray diffraction (XRD)

Powder XRD is a nondestructive tool used to obtain the information about interlayer spacing, structural strain and the impurities in MWCNTs. It was used to monitor the structural modification and changes in lattice strain of the irradiated samples. Bruker D8-Advanced tools XRD was used to characterize the sample.

### 2.6 Laser micro Raman spectroscope

A laser micro Raman (Jovin Yvon, Triax 550) in the backscattering mode equipped with 488 nm blue laser (Argon) and a CCD detector coupled with a monochromator having the XY step resolution of 0.1 μm, wave number accuracy of ± 1 $cm^{-1}$ and its resolution is 0.5 $cm^{-1}$ was used to study the irradiation induced defects on the surface of MWCNTs.

## 3 Results and discussion

In order to understand the influence of irradiation on the structure of MWCNTs at different doses, different analytical techniques were used. The FTIR spectra of MWCNTs after gamma irradiation at different doses such as 25, 50, 75 and 100 kGy are shown in Figure 1. It is observed that the position of all the prominent peaks remains unchanged even after irradiation except for the peak corresponding to C=C. It is appeared at 1576 $cm^{-1}$ for an unirradiated sample, and shifted to 1603 $cm^{-1}$ upon irradiation, which is represented by a dotted line in Figure 1. The shift in peak may suggest a change in the structure of MWCNTs, Zhang et al. (2003), which may have resulted due to the impingement of high energy γ photons on the MWCNTs surface during the irradiation process. Such change leads to the generation of defects on MWCNTs. The formation of defects on MWCNTs during irradiation was confirmed by quantitatively and qualitatively using XRD, Raman spectroscopy and TEM techniques.

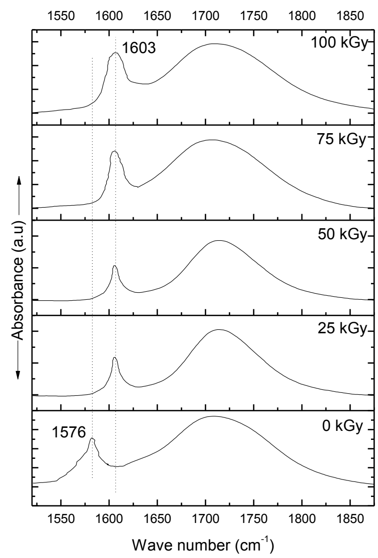


Figure 1. FTIR spectra of gamma irradiated MWCNTs at different doses

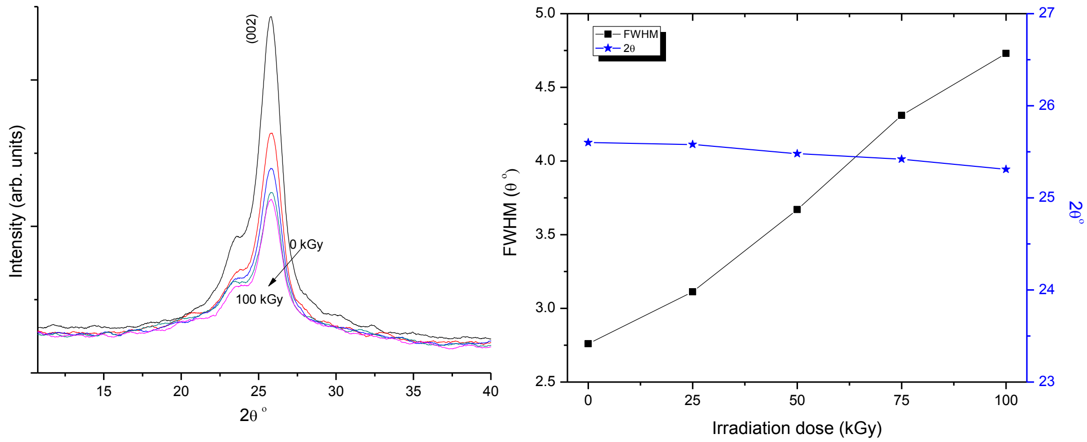


Figure 2. (a) X-Ray Diffractogram and (b) FWHM and peak position of MWCNTs at different irradiation doses

Figure 2a shows the X-Ray Diffractogram, where it is observed that the intensity of the peak corresponding to (002) plane was reduced with an increase of irradiation dose. Figure 2b shows that the full width at half maximum (FWHM) of the sample was increased from 2.76$^o$ for unirradiated sample to 4.73$^o$ for 100 kGy irradiated sample. An increase of FWHM indicates micro straining of the MWCNTs, which confirmed the generation of defects in the structure, Singh et al. (2010). It is also observed that the variation of diffraction angle is considered to be negligible against irradiation dose.

Raman spectroscopy technique was used to confirm the irradiation induced defects on MWCNTs by quantitative analysis. The assessment of defects on the surface of MWCNTs was done by calculating the ratio of the intensity of the defect induced double resonant D band and the in-plane vibration of $sp^2$ carbon atoms resulting in G band, i.e. ($I_D/I_G$), from the Raman spectra of MWCNTs, Mu et al. (2009). The $I_G/I_D$ ratio of irradiated MWCNTs is shown in Figure 3. The $I_G/I_D$ ratio of MWCNTs was reduced from 2.12 for unirradiated sample to 1.03 at 100 kGy irradiation dose, where a linear trend between the $I_G/I_D$ ratio and the irradiation dose was observed as shown in Figure 3. The defects are usually formed on the surface of MWCNTs during their synthesis process due to disordered carbonaceous and amorphous carbon compounds, which contributed to the Raman peaks in the spectra, Pimenta et al. (2007).

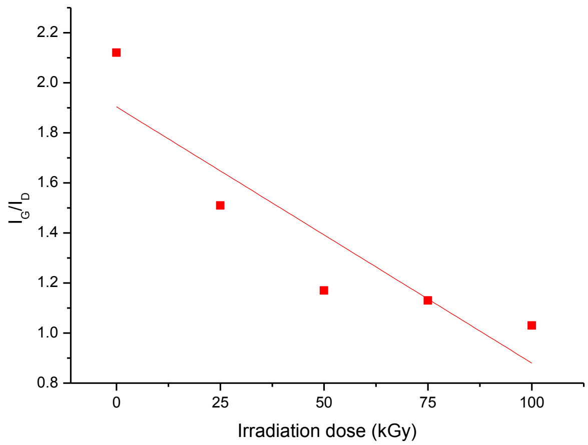


Figure 3. $I_G/I_D$ ratio of MWCNTs at different irradiation doses

A decrease of $I_G/I_D$ ratio indicates that the number of defects on the MWCNTs surface decreased with irradiation dose. Higher $I_G/I_D$ indicates that carbon nanotubes have higher graphitization order, indicating lesser number of defects, but as the irradiation dose increased the disorder of the nanotube structure has increased, which lead to reduction of reduction of graphitization and hence $I_G/I_D$.

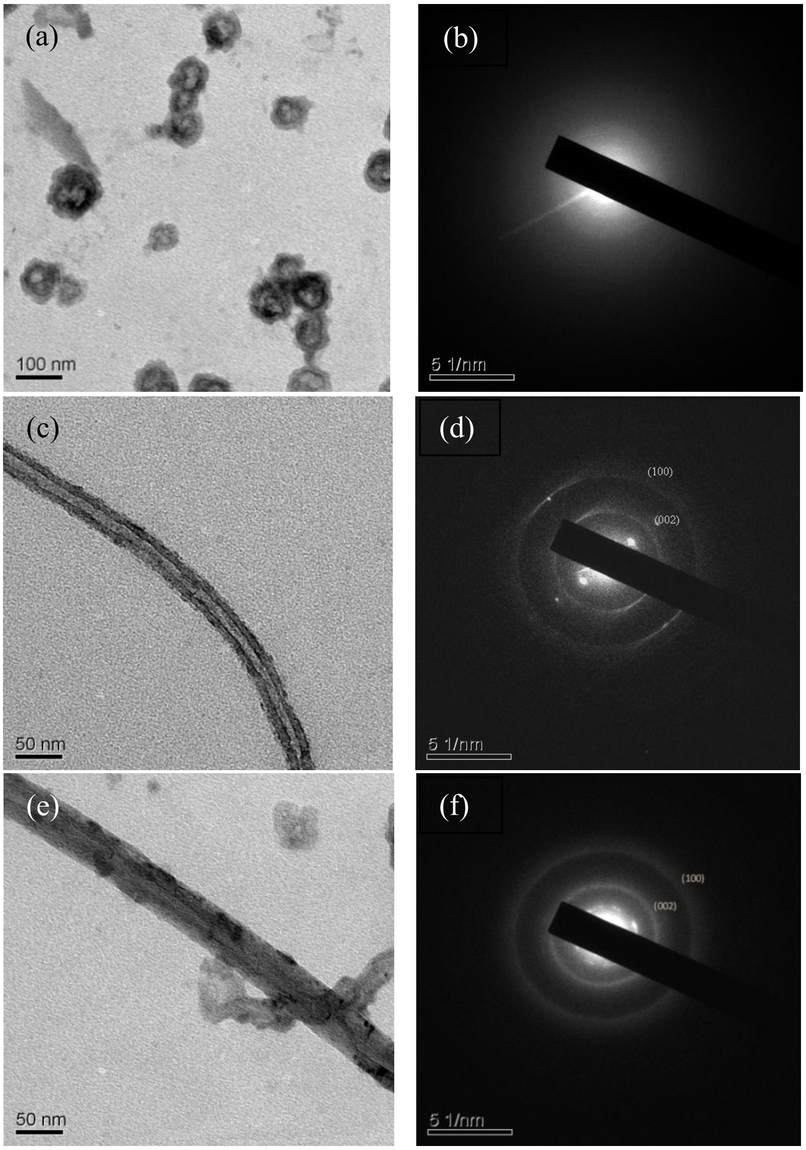


Figure 4. a) Amorphous carbon in untreated MWCNTs b) SAED pattern of (a) c) Chemically treated MWCNT d) SAED pattern of (c) e) 100 kGy irradiated MWCNT f) SAED pattern of (e)

The formation of defects on the surface of MWCNTs is due to the fact that the gamma irradiation in solids caused radiolysis leading to occurrence of various chemical reactions and ionization. The damage induced mechanism was caused by the high kinetic energy electrons ejected from the atoms by γ-photons, which led to the formation of interstitial atoms and other kind of defects, Cataldo (2000). Figure 4 shows the TEM micrographs and Selective Area Electron Diffraction (SAED) patterns of untreated, chemically treated and gamma irradiated MWCNTs. Figure 4a shows the untreated MWCNTs, where the presence of amorphous carbon is observed prominently. The SAED pattern of untreated MWCNTs is shown in Figure 4b, where a diffused halo pattern was observed indicating the presence of large quantities of amorphous carbon. Figure 4c shows MWCNT after chemical treatment, which removed the amorphous carbon and traces of substrate metallic impurities from it and thus the SAED pattern showed a sharp ring pattern. It is shown in Figure 4d, where the prominent (002) and (100) planes are also observed. Figure 4e shows the 100 kGy irradiated MWCNT, which showed the presence of amorphous carbon on the outer walls of MWCNT. The SAED pattern of irradiated MWCNT is shown in Figure 4f, where it is observed that the sharpness of the ring pattern was reduced compared to that of the results observed in Figure 4d. It indicates that the amorphous content was increased in the MWCNTs after the irradiation process due to the damage on their structure.

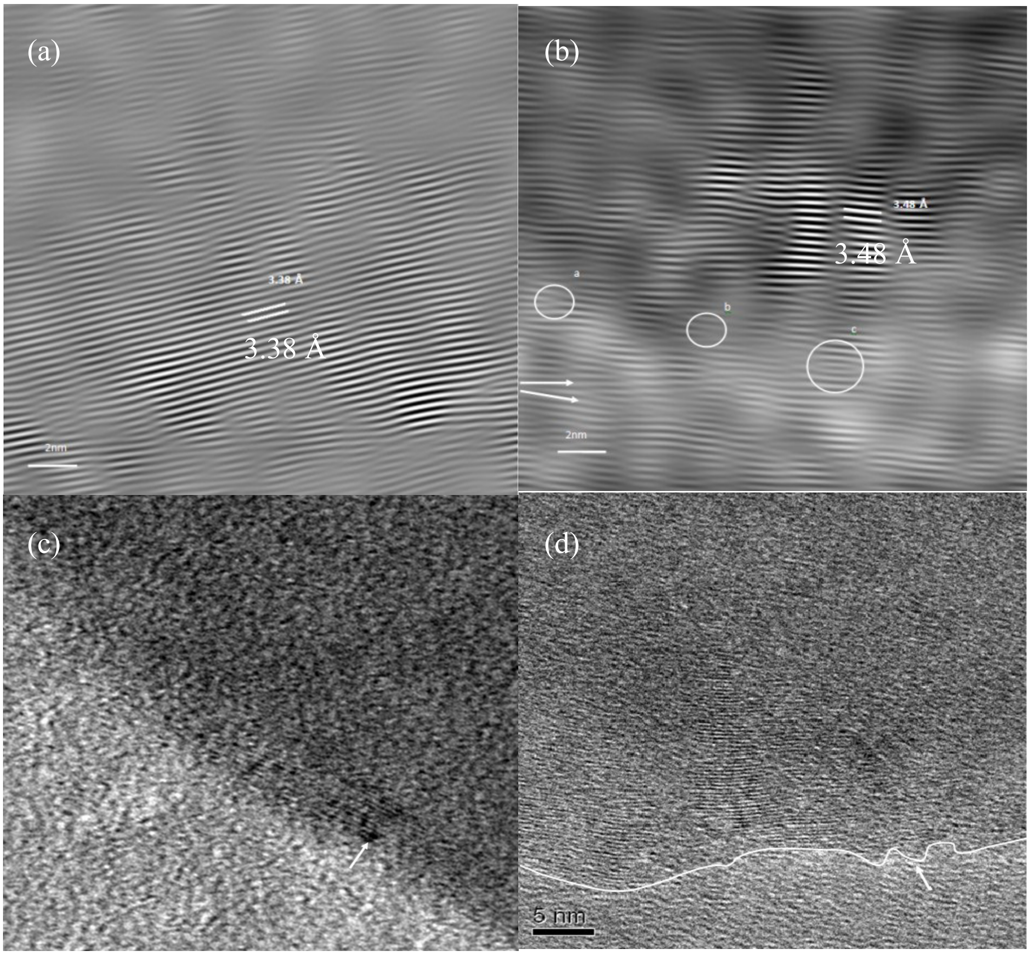


Figure 5. a) Interplanar spacing of (002) plane in an unirradiated MWCNT b) Interplanar spacing of (002) plane and the defects in 100 kGy irradiated MWCNT c) Amorphous carbon on the outer walls d) Damage on the outer walls and the formation of curved graphitic structure after 100 kGy irradiation

In order to visualize the formation of defects, the surface of MWCNT was observed under HRTEM. Figure 5a shows the interplanar spacing of unirradiated MWCNT, where it is observed that the interplanar spacing was found to 3.38 Å and most of the planes are found to be perfect without any distortion. Figure 5b shows that the interplanar spacing of 100 kGy irradiated MWCNT was increased to 3.48 Å. The defects in the planes are shown in the encircled regions, as a, b and c. The changes in the orientation are also indicated by arrows confirming the distortion of the structure of MWCNT due to irradiation. Figure 5c shows the damages on the outer walls of MWCNT and the formation of amorphous carbon, indicated by the arrow. Figure 5d shows the defects or vacancies on the outer wall of MWCNT, indicated by an arrow. The formation of curved graphitic structure also confirms the structural changes on the MWCNT surface.

Figure 6 shows the typical irradiation generated defects on MWCNT at 50 and 100 kGy doses. Figure 6a shows the MWCNT irradiated at 50 kGy**,** where the negative inclination indicated the presence of heptagon ring or various ring members resulting the formation of curvature of sharp bend, Ebbesen (1997). It is also clearly observed that the diameter of the nanotube varied considerably after the sharp bend. It can also be noted that the deposition of amorphous carbon at the vertex of the bend is observed indicating a major structural damage and modification of MWCNT due to the irradiation**.** A similar type of observation can also be seen in Figure 6b, where a local modification of the pheriphery was occurred, and indicated by arrows. Such local modifications in the pheriphery of nanotubes occured due to tetra vacancy collapsing into 5-7-7-5 ring structure, Krasheninnikov et al. (2007). Figure 6c shows a wide variety of defects such as sharp $90^{o}$ bends, variation of diameter, indicated by arrows labeled as 'a' and 'b', and the deposition of amorphous carbon at the sharp bends of 100 kGy irradiated MWCNT. Figure 6d shows a severely damaged MWCNT irradiated at 100 kGy dose. Zig-zag bends were observed indicating the damage and the presence of defects. Such bends with different angles were formed in the presence of various ring members, and such sharp bends were resulted due to the presence of tetragonal rings or vacancies, Ouyang et al. (2001). There is also a finite possibility of the formation of point defects, which are difficult to observe under TEM.

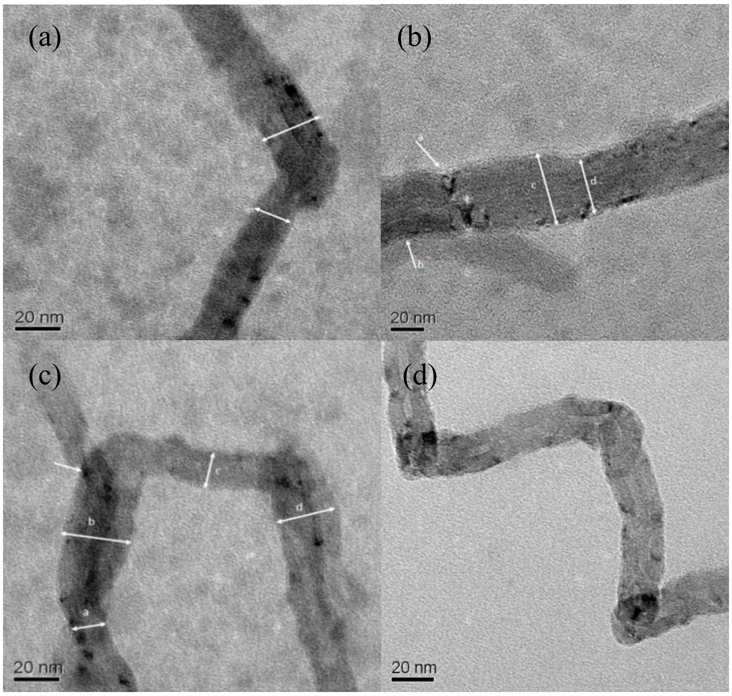


Figure 6. Formation of defects on gamma irradiated MWCNT at 50 and100 kGy irradiation doses (a,b - 50 kGy and c,d - 100 kGy) a) Sharp bend and sudden variation of diameter b) Surface defects and variation of diameter c) Variation of internal diameter d) Zig-Zag bends

It is understood from the above discussion that irradiation has produced defects on the surface of MWCNTs and that the intensity of defects observed also increased with irradiation dose. It has been systematically studied and experimentally proved that the defects on the MWCNTs increased with irradiation. The crystallinity of the MWCNTs also increased with chemical treatment as observed in the SAED patterns. When composites of MWCNTs were subjected to irradiation, these defects act as sites for pinning to the substrate and thus enhance the mechanical properties of the composites. The effect of irradiation on the matrix and MWCNTs reinforcement is completely different and a synergy between these two will aid in over all improvement of the properties.

## 4 Conclusions

MWCNTs were chemically treated and they were gamma irradiated at different doses.

- Irradiation led to the formation of defects on the MWCNTs surfaces.
- Chemical modification of MWCNTs increased their crystallinity, but irradiation has reduced it due to genertaion of amorphous carbon.
- The shift in FTIR peak confirmed the change in the structure of C=C bond in MWCNTs.
- The $I_G/I_D$ ratio of Raman spectra confirmed the reduction of graphitization of MWCNTs with irradiation dose.
- XRD studies revealed that the MWCNTs were subjected to microstrain due to irradiation which led to formation of defects.
- TEM studies showed that the‘d’ spacing of (002) plane increased with irradiation dose. Typical defects on MWCNTs such as formation of amorphous carbon on the outer walls and formation of curved graphitic structure after irradiation were observed.

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