Gamma-irradiation influence on the mechanical and electrical properties of epoxy and nanocomposites.

L Bassiouny[1] and A Anwar[2]

[1] Faculty of Engineering, Misr for Science and Technology, Cairo, Egypt.

[2] Faculty of Engineering, Pharos University in Alexandria, Alexandria, Egypt.

[2] ahmad.anwar@pua.edu.eg

Abstract. The space environment hazards are becoming harsh as they affect both the mechanical and electrical properties of the polymer-based reinforced fiber materials in spacecraft. The structure materials changes by Gamma-irradiation often deteriorate the epoxy matrix or the epoxy/nano-composite properties. As a result, the effect of gamma irradiation on the mechanical and electrical properties of the selected materials were evaluated. The mechanical properties and electrical resistivity of nanocomposites were studied by a universal testing system (UTS) and Keithley 2635A System Source Meter respectively. Fourier transform infrared (FTIR) functioned to assess the chemical structural variation due to the gamma-ray exposure. Dynamic Mechanical Analysis (DMA) was conducted to obtain the Tan delta, loss and storage modulus of each sample. The result showed enrichment in both the mechanical properties and the electrical conductivity of Epoxy/MWCNT's nanocomposites.

1. Introduction

Spacecraft are subject to charged particles and electromagnetic radiations such as an electron, protons, heavy ions, gamma rays, etc [1]. Radiation exposure may cause a degradation of structural materials properties and endanger the mission of the spacecraft [2]. Space radiation consists of two types: charged particles and electromagnetic radiation [3]. Gamma rays have the maximum energy from any wave within the electromagnetic range and the smallest wavelengths. Also, these rays are induced by either the most energetic and hottest objects in the universe, like supernova bursts, regions surrounding black holes neutron stars and pulsars [4]. Epoxy resin is a common thermosetting material used in space because of its high chemical stability and enhanced mechanical properties [5]. Nevertheless, Epoxy materials have a brittle nature and poor electrical and thermal properties. Therefore, they are not often used in engineering applications. Thus, to overcome this problem, the epoxy matrix is enhanced by adding different compatible materials [6]. By applying such solutions, polymeric nanocomposites will combine both the unique factor of the inorganic nanoparticles (such as high aspect ratio, excellent toughness, high strength, good electrical and thermal conductivities) and the functionalities of polymer matrices like easy operability and low cost. [7].

In 2017, a study by Ahmed Alzahrany and Biqiong Chen investigated the influence of reduced graphene oxide (RGO) on the mechanical, thermal and electrical properties of epoxy. The epoxy/RGO nano-composites were obtained by blending both ingredients with a tetrahydrofuran solvent. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction

(XRD) were used to characterize the structure and the morphology of the graphene-based nanosheets and nanocomposites. The findings indicate that the mechanical, electrical and thermal properties of the epoxy matrix were improved after the reduced graphene oxide was inserted [8]. Moreover, In 2021, Olfat A Mahmood et al. demonstrated the effect of various weight percentages of MWCNTs on the mechanical and physical properties of epoxy nanocomposites. The existence of MWCNTs nanoparticles inside the epoxy matrix was achieved by the ultrasonic mixing method. Scanning electron microscope (SEM) and Fourier Transform Infra-Red (FTIR) were applied to evaluate the dispersion of different MWCNTs concentrations in the epoxy matrix. Mechanical properties were obtained by tensile and impact tests. Result revealed that the mechanical, electrical conductivity properties and thermal conductivity coefficient were increased when the concentration of MWCNTs was less than 2wt. % [9].

Also, in 2021, an article by Xing et al evaluated the effect of gamma irradiation on the structure, physical, and mechanical properties of a series of tetra functional epoxies modified DGEBA/DDS. The irradiation sample showed a decrease in the glass transition sample and chain scission. Also, the reduction of the mechanical and thermal properties of the epoxy matrix [10].

In this article, the influence of gamma rays on the mechanical and electrical properties of neat epoxy, and nanocomposites were investigated. Multi-wall carbon nanotubes (MWCNTs) and reduced graphene oxide (RGO) at various weight percentages (0.5wt%,0.3wt%) respectively were dispersed inside the epoxy matrix to increase their mechanical and electrical properties after gamma irradiation.

2. Experimental work

2.1. Material used in these nanocomposites consists of two parts:

2.1.1. The Epoxy matrix. It was bought from Sika Deutschland GmbH company; it consists of two compounds: the resin CR82 and the hardener CR80-6.

2.1.2. The nanoparticles used in this article consist of two sets. MWCNTs and Reduced graphene oxide because both materials are allotropes of carbon that have similar mechanical and electrical properties [11].

The first set was the Multi-wall Carbon nanotubes (MWCNTs) that were manufactured through a high-efficiency catalytic method based on chemical vapour deposition (CVD). These MWCNTs were obtained from the Egyptian Petroleum Research Institute with an inner mean diameter of (4nm), an average external diameter of (8-10 nm), between (5-10 μm) length and a purity exceeding 90%. The mentioned dimensions were identified by transmission electron microscopy (TEM).

The second set consists of three different types of reduced graphene oxide (RG24N, RG270, RG33C) with different reduction techniques were dispersed in the epoxy resin. As known, the reduction techniques affect the carbon/oxygen ratio which disrupt the structure of graphene and reduce significantly the stiffness and strength of reduced graphene when the oxygen content increases [12]. All reduced graphene were confirmed by scanning electron microscopy (SEM).They were made at The City of Scientific Research and Technological Applications in Alexandria.

- RG24N is manufactured by thermal separation of unwanted polyethene tetra-phthalate (PET) bottles with urea at 800˚C for 5 hours. Also, Nitrogen-doping of 3D structure was used to reduced graphene oxide. The atomic structure of the resulting reduced graphene is 83.3% C, 13.9% O and 2.8% N [13].
- RG270 is made by hydrothermal treatment of glucose solution under mild synthesis conditions. Moreover, it is a Nitrogen-doping multi-layered graphene Nano-sheet with an atomic composition is 89% C, 7.2% O and 3.8% N [14].
- RG33C is a green compound of graphene achieved from the recycled PET bottle waste for use in adsorption of dyes in a water solution. The atomic configuration of RG33C is 90.49% C, 2.131% H and 7.379% O [15].

2.2. Preparation of Nanocomposites sheets:

2.2.1. The nanocomposite solution: First, a 50g Epoxy resin was blended with both sets of nanoparticles (MWCNTs and RGO) at altered percentages (0.5 and 0.3) by weight respectively. The blend was stirred manually for 5min at room temperature. Then a Sonicator was used for one hour stetted at 9 kHz frequency and about 750W power for homogeneous diffusion of the nanoparticles in the epoxy resin. Secondly, 27 wt.% of epoxy hardener; the second part of the epoxy matrix; was added to the epoxy/nanoparticle mixture.

2.2.2. The nanocomposites sheet. First, a waxed glass sheet with edges masked with double-faced tape was used to roll an even layer of epoxy/nanoparticle mixture on it. Then a bidirectional high-modulus carbon fiber (Thornel^{TM} T300-3K) with a 0.4 mm thickness layer was placed on the epoxy/nanoparticle film. A four layers sample with a thickness of about 1.8 mm was manufactured to simulate the spacecraft structure. This procedure was repetitive three times after that single layer of foam was adjusted to absorb the excess resin used. Furthermore, the entire glass was covered with vacuum bags and tightly sealed. Lastly, the entire product was vacuumed to (0.5x10-3) bar at a temperature of (45℃) for (24 hr). The final nanocomposite sheet with 2.4 mm thickness was founded to contain four plies of carbon fiber.

3. Evaluation method

Each and every sample was irradiated at a 500 kGy constant dose computed by SPENVIS® software with respect to European cooperation for space standardization (ECSS). A gamma irradiation cell that contained (Co60) Cobalt radioactive source was used at the National Center for Radiation Research and Technology, Cairo, Egypt. The test was executed inside the radiation cell in the existence of air with a dose rate of 2.08 kGy/h at room temperature. The irradiated samples were exposed to gamma rays for about 10 days to reach the total dose of 500 kGy..

The nanocomposite sheets' behaviors were tested mechanically and electrically twenty-four hours after irradiation completion, with respect to the American Society for Testing and Materials (ASTM) and attributed to the polymeric matrix-based composite fabrication standard. Also, Fourier Transform Infra-Red (FTIR) test was conducted in the Military Technical Collage by a spectrometer (JASCO 6600) to evaluate the results obtained from both the tensile and electrical tests prior to and post irradiation with respect to the chemical structure obtained. Furthermore, the Dynamic Mechanical Analysis (DMA) was executed in the Egyptian petroleum research institute by Triton® Technology to evaluate the viscoelastic properties of each sample. The loss modulus and the storage modulus were determined to calculate the glass transition temperature (Tg). Also, the damping factor was measured to indicate the amount of energy absorbed by the material.

4. Results

4.1. Dynamic Mechanical Analysis (DMA)

The loss modulus determines the viscous region of neat epoxy and epoxy/nanoparticles before and after gamma irradiation. Before gamma irradiation, the loss modulus increased for the epoxy/ MWCNT's sample and remained the same for epoxy/RG samples. However, after irradiation, this result was reversed as shown in Figure 1. The loss modulus increased for epoxy/RG samples and showed no significant change in loss modulus for epoxy/MWCNT's sample. This means that the mechanical properties were reduced due to gamma irradiation for the samples containing RG only. Also, this reduction is clearly identified from Figure 1 as the curve showed light crosslinks formed and the peak at 60°C indicate the early shift of the samples from the glassy region to the rubbery region. As known, when the rubbery region increases inside any material the glassy region decreases causing the reduction of its mechanical properties [16].

The storage modulus as in versus temperature curve shown in Figure 2 measures the stored energy that demonstrates the material elastic region. Before irradiation, the storage modulus increased for the epoxy/MWCNT's sample and decreased for the epoxy/RG samples. However, after gamma irradiation,

epoxy/RG33C and epoxy/RG24N exhibit the highest increase in storage modulus compared to neat epoxy. This indicates that the mechanical properties were enhanced for these two nanocomposites as the storage modulus was increased due to the difference between the elastic modulus of each nanoparticle added to epoxy resin [17].

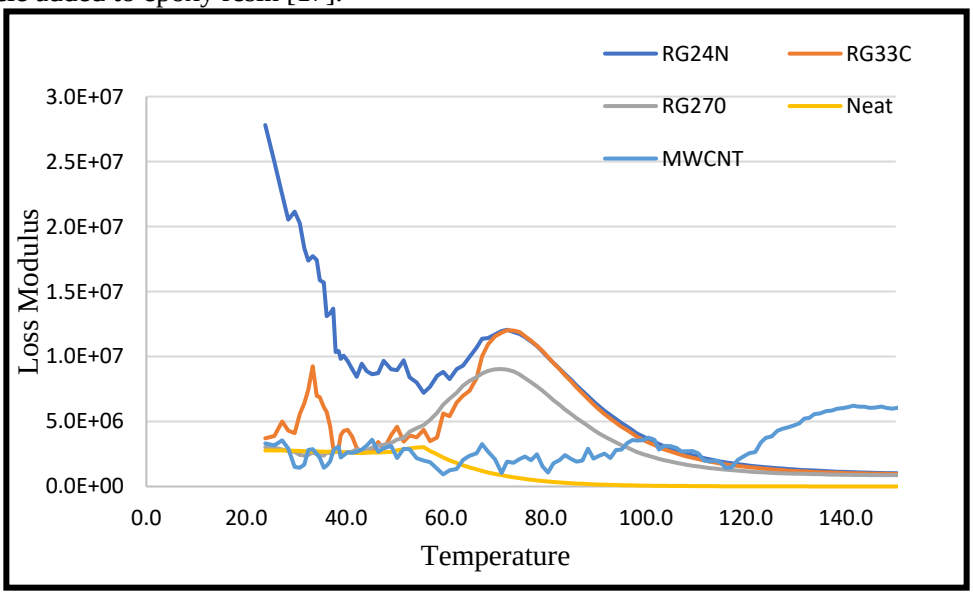

Figure 1. loss modulus for neat epoxy and epoxy/nanoparticles after irradiation**.**

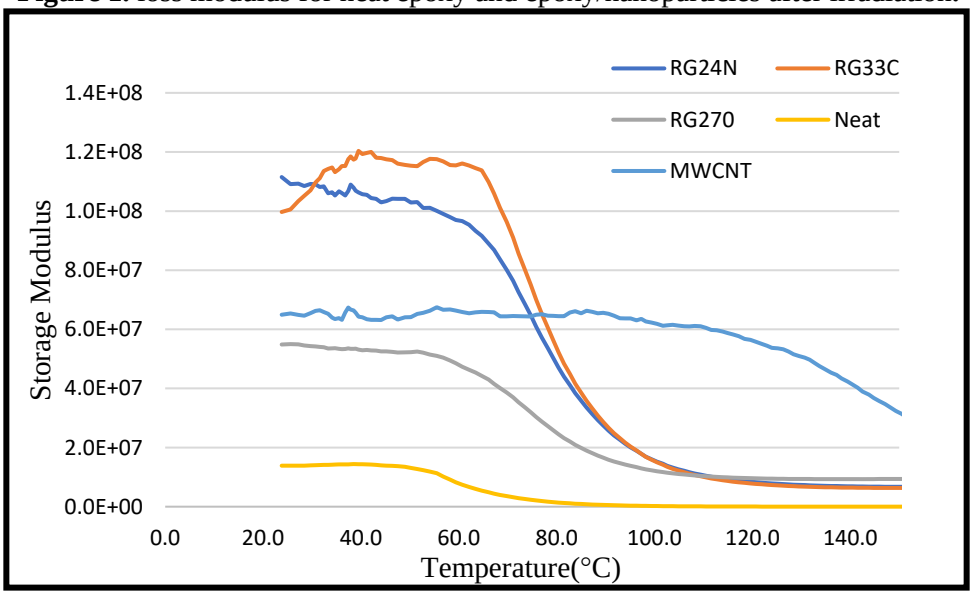

Figure 2. storage modulus for neat epoxy & epoxy/nanoparticles after irradiation**.**

The glass transition temperature (Tg) is obtained by dividing the storage modulus to the loss modulus. Before irradiation; Tg for neat epoxy was 93.17°C while after irradiation, the glass transition for neat epoxy increased to 118°C due to the change of crosslinks inside the neat epoxy existing in both loss modulus and storage modulus graphs. After gamma irradiation, Tg decreased for each and every epoxy/nanoparticle samples as shown in Figure 3. The highest glass transition temperature reduction was obtained by epoxy/G270 of 32% compared to neat epoxy. But, the epoxy/MWCNT's sample showed the lowest decreased in Tg of 13% compared to neat epoxy. The decrease of glass transition temperature could be due to the decrease of crosslinks mentioned before in Figure 1.

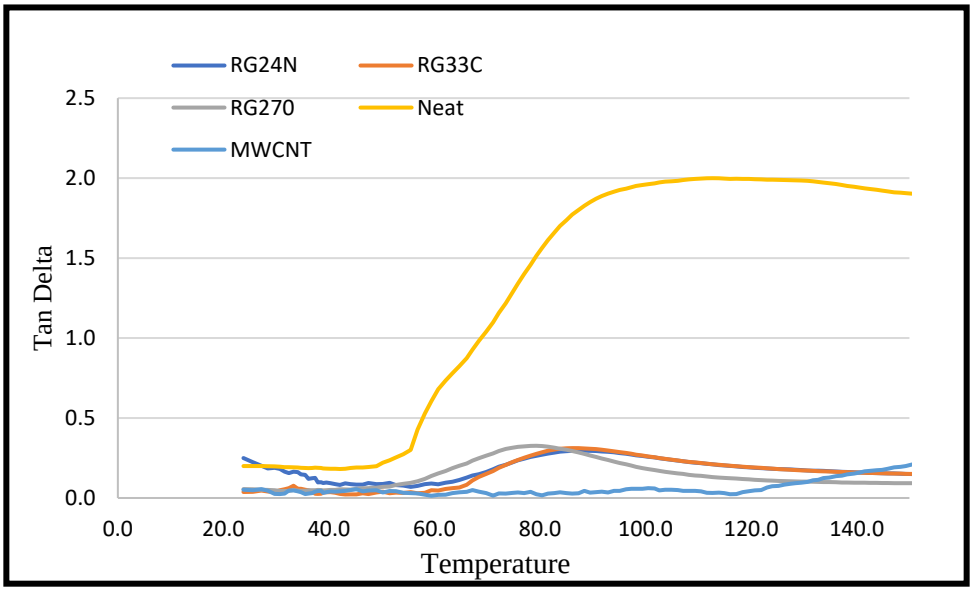

Figure 3. Tangent delta for epoxy and epoxy/nanoparticles after irradiation

4.2. Mechanical Test

The mechanical behaviour of epoxy/nanoparticles and neat epoxy were tested by a testing machine 810 Material Test System (MTS). The tensile test was measured along the fiber direction at a temperature of (23°C ± 3°C) and relative humidity of (50% ± 10%) according to the test standard ASTM D3039. Tensile test investigated the mechanical behaviors (elongation, young's modulus and tensile stress) of Epoxy/Nanoparticles and neat epoxy either before and after exposure to gamma radiation.

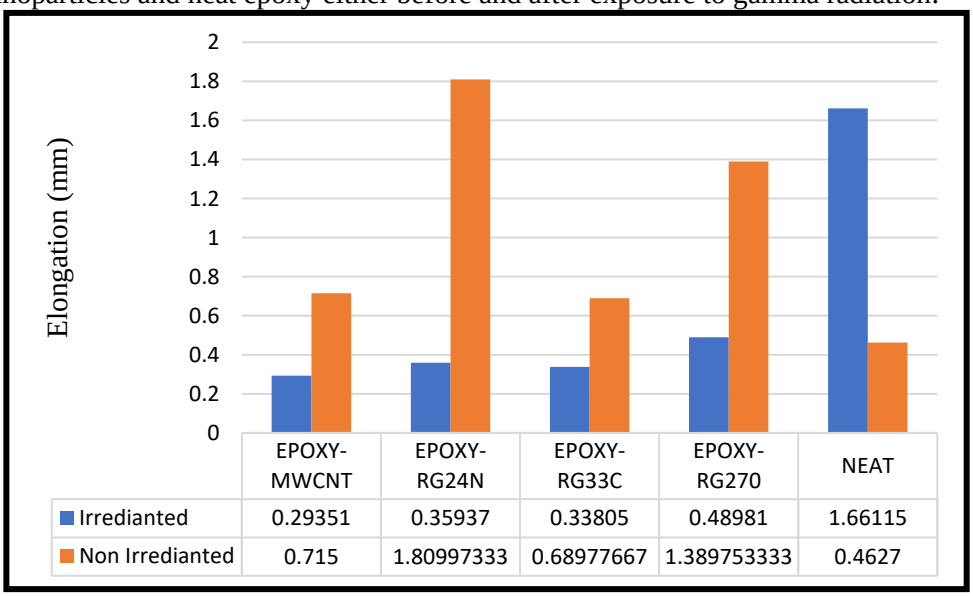

Figure 4. Elongation of non-irradiated and irradiated samples

As presented in Figure 4, The elongation of neat epoxy was strengthened following the nanoparticles dispersion. However, post irradiation; the elongation of all samples was reduced and the highest reduction was obtained by Epoxy/RG24N about 80%. In Figure 5, The young's modulus of neat epoxy and Epoxy/nanoparticles were illustrated before and after gamma irradiation. The young's modulus of non-irradiated samples decreased after the nanoparticles' addition. Also, after irradiation, all samples showed young's modulus decrease compared with irradiated neat Epoxy.

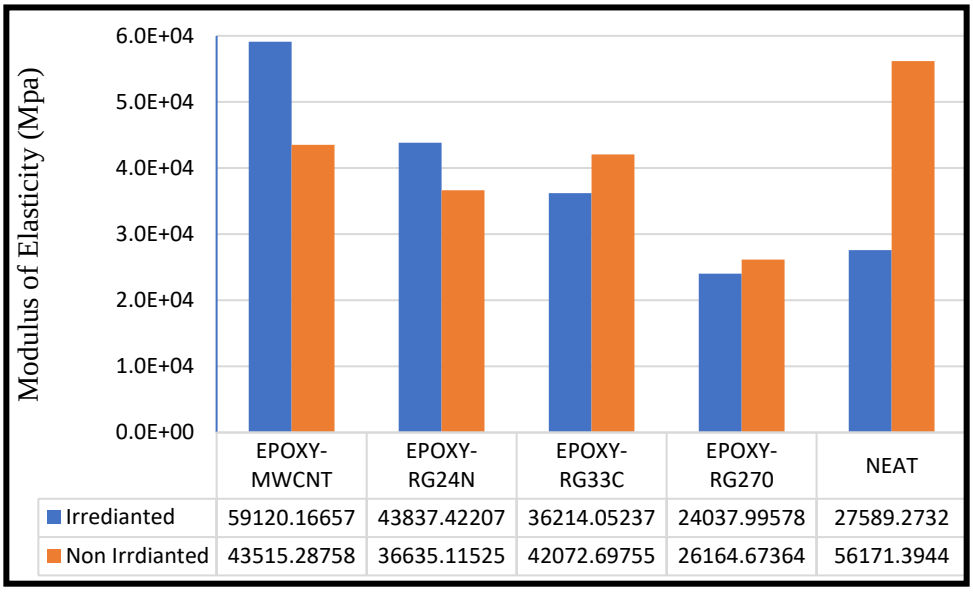

Figure 5. Modulus of elasticity for the irradiated and nonirradiated samples

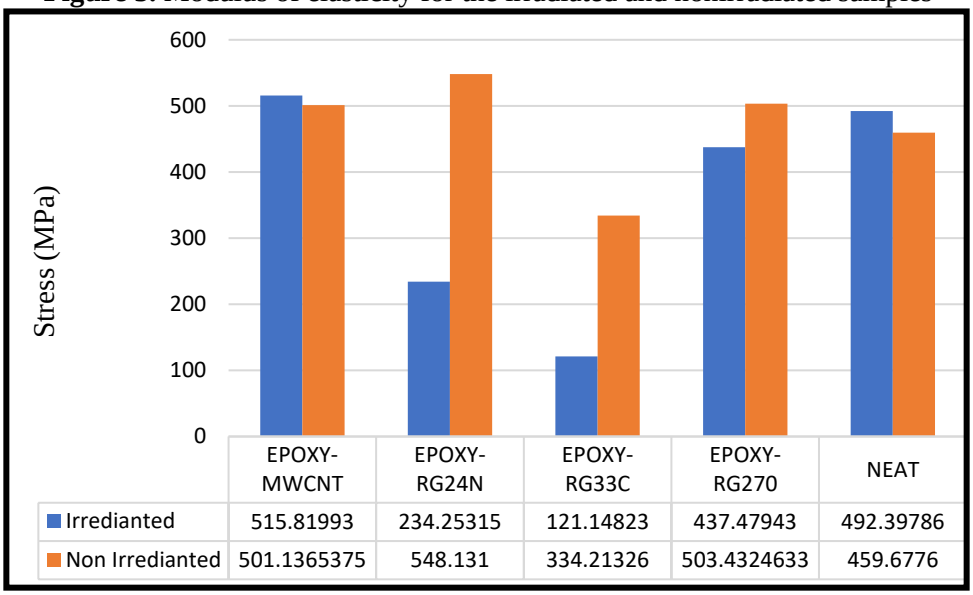

Figure 6. Tensile stress of irradiated and nonirradiated samples

Figure 6 shows that the tensile stress increased after the addition of nanoparticle expect for Epoxy/RG33C. This indicates that the dispersion of nanoparticles enhanced the mechanical behavior of neat epoxy [18]. Moreover, post irradiation; the Epoxy/MWCNT's and neat epoxy showed an increase in the tensile stress. As mentioned, this could be due to the chemical enhancement of epoxy resin as new bonds such C=O was obtained after gamma irradiation [19]. Also, proven from the FTIR analysis of Epoxy/MWCNT's the existence of C=O at 1700 cm^{-1} that could be due partial oxidation formed by gamma irradiation. However, Epoxy/RG nanocomposites showed a decrease in tensile stress by about 57%, 64% and 13% respectively for epoxy/RG33C, Epoxy/RG24N and Epoxy/RG270. This could be due to change of the functional group in the chemical structure obtained from FTIR analysis as the peak "NH_2"that exist due to nitrogen doping completely disappeared after gamma irradiation forming a much sample and flexible structure.

4.3. Electric Test

Electrical resistivity of each specimen before and after Gamma radiation is shown in Table 1 and was measured by Keithley 2635A System Source Meter. Resistivity is a measure of the resistance of a given size of a specific material to electrical conduction. This method was used to calculate the electrical conductivity by $\frac{L}{R*A}$ of neat Epoxy and Epoxy/nanoparticles. Where (L) is the thickness in cm, (R) is the resistivity in ohms, (A) subjected area = 0.502655 cm^2 and (σ) is the electrical conductivity S/cm.

Table 1. Electric conductivity before and after Gamma irradiation

	Resistivity Ω (ohm)		Electrical conductivity (S/cm)	
	Before Gamma irradiation	*After Gamma irradiation*	*Before Gamma irradiation*	*After Gamma irradiation*
Neat Epoxy	0.2076 x10^9	5.054	8.69 x10-9	1035x10-4
MWCNT	7433	6.172	2.54 x10-4	783 x10-4
RG270	669	4.436	3.09 x10-3	116.6x10-3
RG24N	1047	3.934	1.84 x10-3	123.4x10-3
RG33C	957	4.86	2.08 x10-3	107.2x10-3

As shown in Table 1, the electric conductivity of epoxy was improved after the addition of nanoparticles before the gamma irradiation. As the pure Epoxy changed from an insulating material ($\sigma < 10^{-6}$) to a semiconductive material ($10^{-6}<\sigma <10^{-2}$).

The highest electric conductivity is obtained by Epoxy/RG270 nanocomposites. This could be due to the reduction of oxygen inside RG270 which causes the improvement of the electrical conductivity of Epoxy/RG270 nanocomposite [21]. Also, this means that neat Epoxy and RG270 were well dispersed in each other which easily increases the movement of the electric current throughout the nanocomposite causing the improvement of the electrical conductivity. After the gamma irradiation, the electrical conductivity increased of all Neat Epoxy/nanoparticles specimens. However, The Epoxy/RG specimens obtained higher values than the Epoxy/MWCNT 's because gamma rays increased the reduction of oxygen inside the nanocomposite which increased the electric conductivity [22].

4.4. Fourier Transform Infra-Red (FTIR)

The FTIR analysis was applied to assess the functional groups and the chemical structure achieved after the nano-composites irradiation, the whole specimens were submitted to infra-red spectroscopy. FTIR depends mainly on the absorption intensity variation (abs) and the wavenumber. As the higher the wavenumbers the weaker the bond, such as C-H sp3 exists above 3000 cm^{-1} and the smaller the wavenumbers the stronger such as C=O exists at 1700 cm^{-1} [23].

In Figure 7, the FTIR analysis for neat epoxy and epoxy/nanoparticles after gamma irradiation were shown. As demonstrated in this figure, the fingerprint region of each epoxy/nanoparticle and neat epoxy didn't change after irradiation. Even the changes in 400cm^{-1} peak for epoxy/RG24N is considered low IR which is attributed with rotational energy and does not correspond to the molecular structure. This means that the functional groups in the epoxy matrix remained the same.

However, the chemical structure of the rest irradiated changed due to gamma irradiation resulting the reduction of Sp2 c-c bonds existing at 1680 cm^{-1}- 1620 cm^{-1} to SP3 c-c bonds existing at 2990 cm^{-1} -2850 cm^{-1} which results longer bond length and broader peaks as shown in figure above [24].

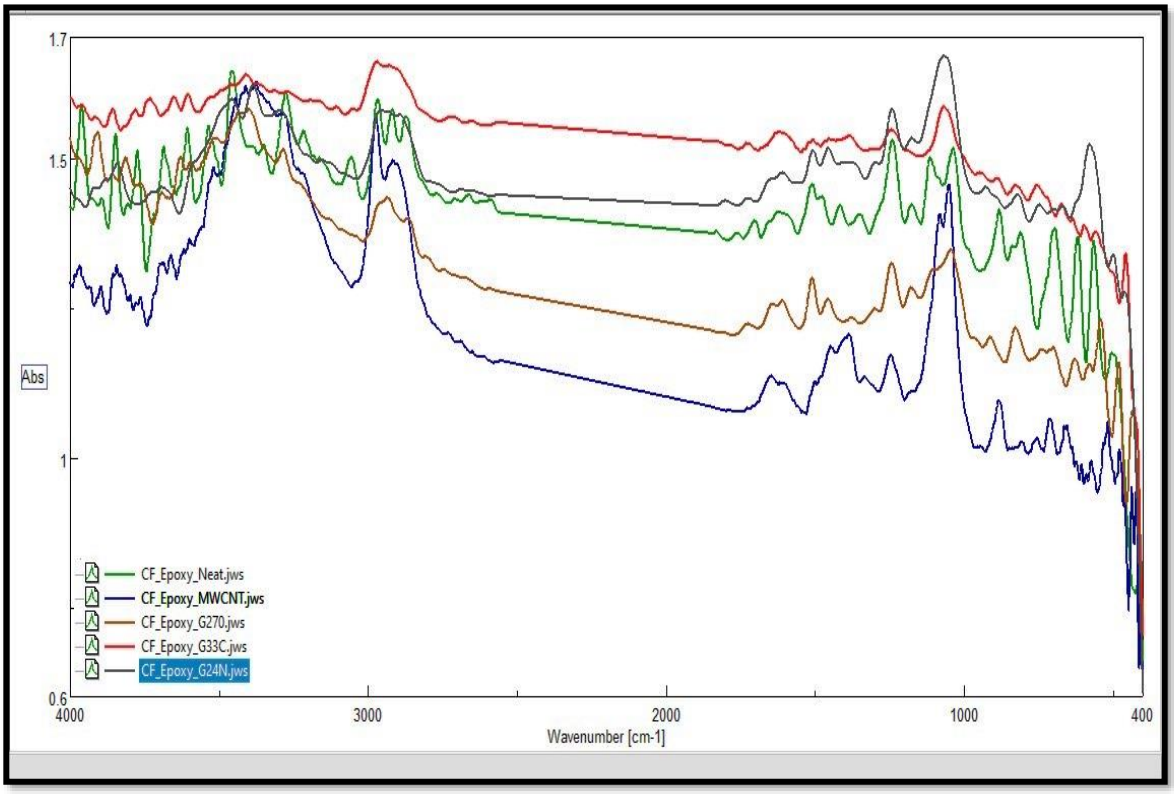

Figure 7. FTIR of all irradiated epoxy and irradiated nanocomposites samples

Table 2 it can notice that, before irradiation, new bonds such as NH2 existed for epoxy/RG24N and epoxy/RG270 nanocomposites as a consequence of the nitrogen doping used to reduce graphene oxide (GO). However, after irradiation these bonds did not exist. This means that the functional groups of Epoxy/RG24N and Epoxy/ RG270 changed to a much sample and flexible structure as gamma rays increased the reduction of both nanocomposites [28].

Table 2. FTIR results before and after irradiation for epoxy and epoxy/nanoparticles nanocomposites.

Bond	Wavelength (cm^{-1}) [2], [19], [20]	Specimens	Wavelength non irradiated	Wavelength irradiated
Finger print	~<1000	Neat Epoxy	421.37	564.077
			608.431	617.109
			715.461	694.248
				882.274
		MWCNT	442.583	436.798
		G33C	410.763	413.656
			574.683	598.789
			727.996	607.467
		G270	424.263	431.977
		G24N	419.442	-
			483.081	456.082
			613.252	584.325
Sp^3 C-H	2850-3000	Epoxy	-	2967.91
		MWCNT	2937.06	2973.7
		G33C	-	-
		G24N	-	2963.09
Sp^2 C-H	3000-3100	Epoxy	3151.11	-
		Epoxy	-	3846.33
			3728.69	3774.01
			-	3685.3
			-	3607.2
			-	3534.88
			-	3452.92
			-	3276.47
O-H	3200-3900	MWCNT	3417.24	3375.78
			3458.71	-
			3855.01	-
			3938.89	-
		G33C	3423.99	-
			3781.72	3647.7
			3907.07	-
		G24N	-	-
		G270	3824.15	-
C=C-H	1607- 1510	Epoxy	1605.45	1510.00
		MWCNT	1594.84	-
		G33C	1598.7	1558.2
NH_2	1590-1650	G24N	1601.59	-
		G270	1599.66	-
N-H	3350-3500	G24N	3406.64	3386.39
		G270	3394.1	3399.89

5. Conclusion

In this article the effect of gamma irradiation on the mechanical and electrical properties were evaluated. It was found that the gamma irradiation dramatically affects the mechanical properties of all epoxy/reduced graphene oxide nanocomposites. This was due to the change of functional group that formed a much flexible material and a much sample chemical structure demonstrated by FTIR analysis. However, for Epoxy/MWCNT's the mechanical properties were enhanced due to the new chemical structure obtained as new bonds such as c=o existed after irradiation. On the other hand, the electrical properties of Epoxy/reduced graphene oxide nanocomposites were higher than Epoxy/MWCNT's composites after the resulting reduction from gamma irradiation. Also, the dynamic mechanical analysis showed that all samples were affected by gamma rays revealing a decrease in the mechanical properties and the glass transition temperature of samples with different ranges. This means that gamma rays affect the mechanical and electrical properties depending mainly on the type of nanoparticle used and its atomic composition. Moreover, Epoxy/MWCNT's nanocomposites is more stable to withstand high loads and space radiations than Epoxy/RG nanocomposites.

Therefore Epoxy/MWCNT's nanocomposites are preferred to be used as a primary structure in satellite plates and as an external structure of spacecraft.

References

[1] Zicai S, Yan X, Yuming L, Yigang D and Chunqing Z 2015 Proc. Int. IOP Conf. Series: Materials science and engineering vol 5 Changsha, China p 585.

[2] National aeronautics and space administration (NASA) 2015 Nuclear and space radiation effects on materials Virginia USA p 1-49.

[3] Miller S and Banks B 2010 Degradation of spacecraft materials in the space environment MRS Bulletin vol 35 p 20-24.

[4] Paul S and Sindhu K 2015 A neural network model for predicting the dielectric permittivity of epoxy- aluminium nanocomposite and its experimental validation IEEE Transactions on Components, Packaging and Manufacturing Technology Vol 5 P 1122-1128.

[5] Jiacheng W, Thuc V and Fawad I 2015 Epoxy/graphene nanocomposites – processing and properties: a review J RSC Advances Vol 5 P 73510-73524.

[6] Šupová M, Simha M, Karla G and Cech B 2010 Effect of nanofillers dispersion in polymer matrices: A Review J Science of Advanced Materials Vol 3 P 1-25.

[7] Ahmed A and Biqiong C 2017 Effect of reduced graphene oxide on the mechanical, thermal and electrical properties of epoxy J of Material Sciences & Engineering vol 6 P 149.

[8] Olfat A, Zainab N and Hind W 2021 Effect of Different Multi-Walled Carbon Nanotubes MWCNTs on Mechanical and Physical Properties of Epoxy Nanocomposites Proc. Int. IOP Conf. Series: Materials science and engineering vol 1094.

[9] An X, Yu B, Yinghong W, Fazhan Z, Yan M and Xiaoyu L 2021 Effects of γ irradiation on thestructure, physical and mechanical properties of a series of tetrafunctional epoxies modified DGEBA/DDS J Materials Today Communications Vol 27

[10] Berhanuddin, N, Zaman I, Rozlan S, Karim M, Manshoor B, Khalid A, Chan S and Meng Q 2017 Enhancement of mechanical properties of epoxy/graphene nanocomposite Proc. Int. IOP Conf. Series: Materials science vol 914.

[11] Gagan K, Raju A, Peter C, Mark B and Pathiraja G 2015 Electrically conductive polymers and composites for biomedical applications J RSC Advances vol 5, p 37553-37567.

[12] Sanjeev R, Jahnavee U, Kyriaki P, Rehan U and Raj D 2018 Reduced graphene oxide: Effect of Reduction on electrical conductivity J composites science, vol 2 p 1-12.

[13] Kianfar S, Nozad G and Zarenezhad B. 2022 Experimental and artificial intelligence for modelling the cyclic voltammogram behavior of Pt/reduced graphene oxide nano-catalyst synthesized using gamma irradiation at different experimental conditions of graphene oxide J Solid State Electro-chem Vol 26 P 2195–2207.

[14] Ansón-Casaos A, Puértolas J, Pascual F, Hernández-Ferrer J, Castell P, Benito A, Maser W and Martínez M 2014 The effect of gamma-irradiation on few-layered graphene materials J Applied Surface Science vol 301 P 264-272.
[15] Gonzalez M, Cabanelas J, Baselga J, 2012 Applications of FTIR on epoxy resins - identification, monitoring the curing process, phase separation and water uptake P 261-270.
[16] Ruslinda R 2014 Surface functionalization of multiwalled carbon nanotube for biosensor device application proc. conference of semiconductors electronics.
[17] Eko A, Shoerya S, Gatot S, and Sadur R 2016 Facile synthesis of graphene from graphite using ascorbic acid as reducing agent proc. in AIP conference Publishing Vol 1725.
[18] Shamellia S, Abdul Rahman I, Ahmad A, Mohd H, Mohamed F, Radiman S, Yasir M, Sarmani S, Ayob M and Ahmad B 2015 Reduction of graphene oxide to graphene by using gamma irradiation Vol 19 P 1223-1228.
[19] Noha El Essawy, Safa M, Hassan A, Abdelaziz H, Mohamed A and Hesham A 2017 Green synthesis of graphene from recycled PET bottle wastes for use in the adsorption of dyes in aqueous solution J Ecotoxicology and Environmental Safety Vol 145 P 57-68.
[20] Bazrgari D, Moztarzadeh F, Sabbagh-Alvani A, Rasoulianboroujeni M, Tahriri M and
[21] Tayebi L 2018 Mechanical properties and tribological performance of epoxy/Al2O3 nanocomposite J Ceramics International Vol 44 P 1220-1224.
[22] Jiachen W and Inam F 2017 Processing of epoxy/graphene nanocomposites: effects of surfactants J Polymer Science & Applications Vol 1
[23] Djouani F, Zahra Y, Fayolle B, M. Kuntz and Verdu J 2013 Degradation of epoxy coatings under gamma irradiation J Radiat. Phys. Chem Vol 82 P 54-62.