Synthesis and Characterization of Gamma Irradiated Graphene Oxide-Polypyrrole Nanocomposites

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Abstract: Variations in crystalline structure, optical property, structural bonding in Graphene Oxide (GO) doped polypyrrole (PPy) under gamma irradiation at 100 KGy with effective dose rate of 2.86 KGy per hour have been studied. The crystalline structure has been studied utilizing XRD spectroscopy and it has become clear that as compare to non-irradiated, irradiated sample show more shift toward crystalline nature, this is because of the decrease in d-spacing. The variation in optical properties have been evaluated using UV-VIS spectroscopy, it has been pointed that gamma irradiation reduces the optical band gap due to the chemical reactions, such as chain scissioning etc., induced by gamma exposure, this result is further supported by FT-IR spectroscopy.

1. Introduction

Since ancient times, Polymer in its inherent form has been playing a vital role in human life. The eventual polymers that define life were Ribonucleic acids (RNA) and deoxyribonucleic acid (DNA). As the time changes, the way of living and the demand of the people drastically inclined. Therefore a large number of innovations has been undertaken for the development of new polymers than naturally occurring polymers, and it has grown stupendously. The attention of the researchers diverted towards the electrical properties of polymers with the discovery and study of conducting polymers. The significance and prospective influence of this new class of material get recognition by the scientific community in 2000 with the award of Nobel prize to Shirakawa, Heeger, MacDiarmid for their discovery that certain polymers can be chemically modified to conduct electricity. Due to the prior economic and social importance, a large number of research is still going on in this field to find the unfound. These polymers conduct electricity due to the presence of conjugated \(\pi\)-electrons (C=C) that can easily delocalize and determine the electronic properties of conducting polymers. The conductivity of these polymers may be further enhanced by means of doping. Polypyrrole is one of the best contender which has a popularity due to its considerable
electrical and electronic properties. The early history of Polypyrrole (PPy) begins with the work of a famous chemist named Angelo Angeli and dates back in 1915 [1-3] during 1960, Weiss starts its research on semiconducting polymers and reported the resistivity of compressed pallets of polypyrrole lying between 11-200 $\Omega$-cm [4]. It can be settled in both non-aqueous and aqueous medium and can also support various substrates due to its stability and greater conductivity [5]. The most attracting feature of polypyrrole is high ability for the passage of electricity and good stability in oxidized states. Since its discovery, polypyrrole has enormous technological applications such as sensors, batteries, capacitors, actuators, solar cells and electrodes [6-13].

As it is understood that conductivity of polymers can be enhanced by different ways and one of the best ways is doping. A number of researches have reported that PPy shows a noble conducting behavior as it is doped with Graphene Oxide (GO) [14, 15] due to the attractive properties of GO such as splendid electronic conductivity, high intrinsic mobility, larger surface area, thermal stability, high Young’s modulus and structural flexibility [16]. It is also used as a filler for certain nanocomposites such as polyvinyl alcohol, polyester etc, for amplifying the properties of nanocomposites, GO is exfoliated in polymer matrix. This work has been carried out to investigate the gamma irradiation effects on polypyrrole/ graphene oxide composites as these radiations induce rearrangements of atoms and molecules present in the composites. Moreover, this kind of radiation can also cause molecular excitations in polymer that leads to the breakage of bonds and cross-linking. However, researchers have reported the reduction in micro strain, distortion, and dislocation density of Au-PPy composites with increasing gamma radiation dosage [17].

2. Experimental Details

A known Pyrrole has been dissolved in ethanol under constant stirring. Ferric chloride has been added drop wise in solution under constant stirring. The suspension has been kept untouched for a day. It is then filtered and washed using acetone and water respectively. The black precipitates obtained have been dried for hours at 60°C - 70°C in a vacuum oven.

Graphite powder, sodium nitrate and potassium permanganate have been mixed in sulphuric acid in the ice bath under continuing stirring for 3 hours and then in a hot water bath by maintaining a temperature of 40°C for 2 hours. A solution of distilled water and hydrogen peroxide have been added to the hot mixture with prompt stirring for about an hour. The suspension obtained was filtered using filter paper.

Equal amount of GO and Cetyl Trimethyl Ammonium Bromide (CTAB) have been weighed and mixed in distilled water using a magnetic stirrer. The mixture is left for 10-15 minutes and then known amount of PPy is added to the mixture to make the compositions of ratios of Go: PPy as 1:9, 1:4 and 3:7. All solutions have been kept untouched for 24 hours and dried thereafter in a vacuum oven at 60°C.

The composites so obtained have been irradiated to Gamma-rays of a Co-60 gamma source from IUAC, New Delhi with a dosage of 100Kgy at an effective dose rate of 2.86 Kgy per hour. The composites have been characterized for UV-Vis Spectroscopy before and after gamma-irradiation in the wavelength range of 200-800 nm. FTIR Spectral analysis of GO-PPy composites has been carried out before and after gamma-irradiation using Shimadzu 8400 S, in terms of wavenumbers ranging between 4000-400 cm$^{-1}$. X-Rays diffraction analysis of GO-PPy composite has been performed pre and post gamma-irradiation utilizing a PANalytical X’Pert Pro X-ray diffractometer with the 2 theta angle varying between 10° to 90° respectively.
3. Results and Discussions

FTIR Spectral analysis plays an important role in providing information about the bond structure of materials. The FTIR spectra of GO-PPy nanocomposites pre and post gamma irradiation along with pure PPy have been recorded in transmittance mode and have been shown in Figure 1 and 2. The vibrational bands at 776 cm\(^{-1}\) represents the aromatic C-H bond vibrations [18]. A sharp peak at 1044 cm\(^{-1}\) accounted for epoxide group of pure PPy has been shifted to 1036 cm\(^{-1}\) with the addition Graphene Oxide. It reflects the presence of inter hydrogen bonding and \(\pi - \pi\) interaction between GO and PPy moieties. Furthermore, the peak gradually shifted to 1047cm\(^{-1}\) after gamma irradiation indicating the chain scissions produced by gamma rays. The most intensive peaks have been noticed in the range of 1600 to 900 cm\(^{-1}\). A peak at 1734 cm\(^{-1}\) stemmed to C=O stretching [19] has been shifted towards lower wavenumber with addition of GO and transfer further towards lower wavenumber after gamma irradiation. The peaks at 1548 cm\(^{-1}\) and 1444 cm\(^{-1}\) indicating the presence of C=C anti symmetric and symmetric C=C ring stretching respectively [20-21] have not found to move from its position indicating the stability of aromaticity of PPy contrary to addition of GO or gamma irradiation. It is evident from the comparison of Figure 1 and 2 that the intensity of all the peaks increase with the gamma irradiation of the samples to the dosage of 100KGY. Thus it may be concluded that gamma irradiation of the composites induces chain scissions in the bonds associated to the C=O stretching [22-23]. It is also evident from the figures that the intensities of the peaks decrease with the increase in the GO concentration in PPy after gamma irradiations, whereas the reverse trend is observed before the irradiation of the samples.

Figure 1: FTIR spectra of Non-irradiated Samples of PPy and GO-PPy Nanocomposites
Figure 2: FTIR spectra of Gamma irradiated Samples of PPy and GO-PPy Nanocomposites with a dosage of 100KGY.

The UV-Vis spectral analysis have been carried out for pre and post gamma-irradiated (100KGY) PPy-GO composites along with pristine PPy. Figure 3-4 represents UV Vis spectra of PPy-GO composites pre and post gamma irradiation.

Figure 3: UV-VIS spectra of PPy-GO composites
Figure 4: UV-VIS spectra of gamma irradiated PPY-GO composites

It is well known that UV-Vis spectra gives the energy and band gap which can be direct or indirect depending upon the compounds. The band edge has been found to show red shift with the addition of GO in PPy as is evident from figure 3, and shifts to lower wavelength after gamma irradiation. It is detected that the unexposed and exposed Pure PPy and GO-PPy composites have indirect band gap, which has been calculated for all the composites. It is observed that the gamma irradiated samples have lesser band gap as compared to non-irradiated samples. The table given below shows the band gap of non-irradiated and gamma irradiated pure PPy.

Table 1: Variations in indirect band gap of PPy-GO composites before and after gamma irradiation

| PPy-GO composites | Gamma irradiated PPy-GO composites |
|-------------------|-----------------------------------|
| Composition ratio | Indirect band gap energy (eV)     | Composition ratio | Indirect band gap energy (eV) |
|                   |                                   |                   |                               |
| 1:0               | 2.69                              | 1:0               | 1.74                          |
| 9:1               | 1.20                              | 9:1               | 1.00                          |
| 4:1               | 0.80                              | 4:1               | 0.61                          |
| 7:3               | 0.76                              | 7:3               | 0.54                          |

From the above table, it is easily observed that the band gap decreases from non-irradiated to gamma-irradiated samples. It has been observed that the band gap is diminishes with the gamma
irradiation which may be due to the formation of free radicals which can transmit the charge in to the polymer chains. As a result of charge transportation, the increment in the conductivity has been observed [24].

The impact of gamma irradiation is that it shifts the bond formed and revamp them which brings about the ring opening in the unsaturated C=C Bond. So due to the formation of double bond, the band gap may have been decreased in the gamma radiated samples as compared to the non-irradiated samples [25].

3.1 X-Ray Diffraction Studies

The results of XRD analysis of PPy and PPy-GO nanocomposites before and after gamma irradiation have been represented in figure no. 5 and figure no. 6.

![XRD graph of Non-irradiated Pure PPy and PPy-GO Nanocomposites](image)

**Figure 5:** XRD graph of Non-irradiated Pure PPy and PPy-GO Nanocomposites
Figure 6: XRD graph of Gamma-Irradiated Pure PPy and PPy-GO nanocomposites

Major peaks at $2\theta = 14.44^\circ$, 26.38° and 41.19° have been observed for pure PPy indicating the semi-crystalline nature of the PPy. This semi-crystallinity is observed due to the systematic alignment of polymer chain by chain folding. The inter planer d-spacing of 6.1277 nm corresponding to $2\theta = 14.44^\circ$ has been found to reduce to 6.029 nm with the addition of GO to PPy. A new peak has also been observed to originate with the addition of GO at $2\theta = 19.00^\circ$ that may be attributed to the amorphous behavior of GO. The reduced d-spacing from pure PPy to PPy-GO composites leads to the conclusion that GO has penetrated through the interlayer spacing of the polymer [19]. Similar behavior has been observed after gamma-irradiation of the composites. The gamma irradiated PPy showed major peaks at $2\theta = 14.68^\circ$, 26.17° and 41.23° whereas the peaks of GO-PPy composites have been observed at $2\theta = 14.92^\circ$, 42.669°. The inter-planar spacing for gamma irradiated PPy is found to be 6.0289 nm that has been reduced to 5.9262 nm. The d spacing has been found to reduce with gamma irradiation of the composites.

4. Conclusions

The studies conclude that gamma radiations modifies the structure of PPy-GO composites via chain scissions. The UV-Vis results indicate that the band gap of the composites decrease with gamma irradiations and with increased GO concentration in such a manner that the composites may be utilized in semiconducting devices. The linkage containing unsaturated C=O bond may be considered as the weakest linkage. The composites seem to get crystalline after gamma irradiation.
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