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Structural Modifications of Gamma Irradiated Polymers: An FT-IR Study

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ABSTRACT

A comprehensive study of structural modifications of gamma irradiated polymers in the dose range of 10^1 *Gy to* 10^6 *Gy, was conducted using FT-IR technique. The results were varied in nature, proving that all polymers do not undergo similar type of destruction under similar irradiation conditions. The IR spectrum of polypropylene polymer confirmed the total destruction of isotactic arrangements of the polymer. The destruction of the polypropylene polymer lead to the formation of alcoholic and ketonic groups. For polyacetate polymer, elimination of carbon dioxide took place due to destruction of the ester group. Interestingly, for polycarbonate polymer also, it was observed that at the dose of* 10^6*Gy, phenolic group formed due to cleavage of ester bonds. For polyvinyl chloride, there was a clear spectral indication regarding the formation of C=C bond and simultaneous decrease in concentration of C-Cl bond which took place upon gamma irradiation.*

Keywords: FT-IR, Gamma Dose, Polymer.

INTRODUCTION

The study of radiation induced modifications in polymers is a recent yet expanding field of research. Owing to its technological applications, it has received an immense amount of attention and is being extensively investigated. Modifications induced by irradiation may sometimes enable in achieving desired improved physical and chemical properties of polymers, thus modifying them for specific use. Thus the study of polymer modifications which comprises a study of physico–chemical variations in polymers due to irradiation is of great importance [1-15]. These modifications are the result of superimposition of several mechanisms including the interaction of incident particles with matter, causing initiation of different secondary reactions. These changes in polymers depend on the radiation doses, internal structures of polymers such as types of functional groups present, chain lengths, etc. In general, most of the radiation-induced modifications can be traced back to changes taking place in the structure of the parent polymer. Some of the changes have been attributed to the scissoning of the polymer chains by incident ions, breaking of covalent bonds, promotion of cross-linkages, formation of carbon clusters, liberation of volatile species and, in some cases, even formation of new chemical bonds.

It is expected that materials' response to high energy ion-beams is considerably different from those induced by γ-rays. However, unfortunately though most of the works in recent years have been limited to energetic heavy ions, low energy ions and fast electrons, only few works have been reported on gamma irradiation effects on polymers [16-20]. Our group has been working on modifications of polymers by high doses of gamma radiation for last couple of years [21-26]. It is observed that in some cases the changes are very significant and in some case the changes are very negligent. In this paper, a comprehensive analysis of the interesting results observed through IR spectroscopic studies are reported in details.

MATERIALS AND METHODS

Several types of polymers like Polypropylene (PP), Polyvinyl chloride (PVC), Polycarbonate (PC), Polyacetate, Poly Allyl Diglycol Carbonate PADC were studied. Samples of sizes 3×3 cm^2 (seven numbers for each set of polymers) of each type polymer were prepared from commercially available sheets. They were then irradiated with various doses of gamma radiation in the dose range of 10^1–10^6 Gy. The gamma exposure was conducted at room temperature using a ^{60}Co gamma source having a dose rate of 3 kGy/h. The exposure time varied from 12s to nearly 14 days in order to deliver the required doses. The errors in doses ranged from 8% for low doses (10^1 Gy) to about 1% for high doses.
The properties of the polymers studied are given in Table 1.

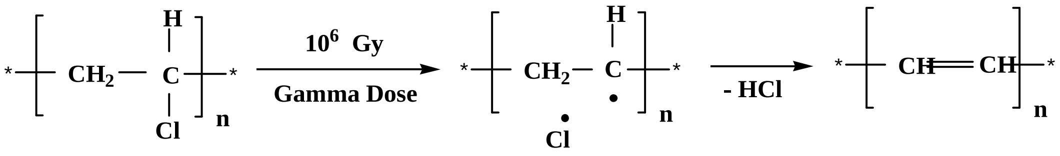
Table 1. Properties of different polymers under study

Name	Common Name	Thickness	Density	Manufacturer
Polycarbonate	PC	100 µm	1.20 g cm−3	Bayer AG, FRG
Polyallyldiglycol carbonate	PADC	1500 µm	1.32 g cm−3	Homalite,USA
Polyallyldiglycol carbonate	PADC	650 µm	1.32 g cm−3	American Acrylics corp.
Cellulose Acetate Butyrate	Triafol-BN	120 µm	1.20 g cm−3	Bayer AG, FRG
Polyvinylchloride	PVC	100 µm	0.90 g cm−3	Commercially Available
Polypropylene	PP	80 µm	0.90 g cm−3	Commercially available

FT-IR spectra of the irradiated and pristine polymers were taken in the solid state. The spectra were recorded using a Nicolet Impact 410 Fourier transforming instrument in the range 4000 cm^{-1} to 400 cm^{-1}. However for polycarbonate polymers having a thickness of 100µm, FT-IR measurements were carried out using an Equinox 55, Bruker IR spectrophotometer.

RESULTS AND DISCUSSION

IR spectra of **polyvinylchloride (PVC) polymer** recorded both before and after irradiation do not give any significant information. Some of the characteristics peaks are totally unchanged even after the gamma exposure. However it can be observed that dehydrochlorination of the polymer takes place, leading to the formation of C=C bonds. This is confirmed by the appearance of IR absorption band at 1620–1680 cm^{-1} (characteristic. of C=C stretching).[22] Intensity of the absorption bands for the C-H stretching vibrations (3100-3000 cm^{-1} region) also reduces for the PVC polymer with increasing gamma doses. These changes are significant at the dose of 10^6 Gy. This signifies that due to gamma exposure, scissioning of C-H bond takes place resulting formation some double bonds. The probable mechanism of structural changes proposed [22] is as follows:



The FT-IR spectra of pristine and irradiated **Polypropylene (PP) polymer** with the highest dose of 10^6 Gy is shown in Fig.1. The characteristics peaks are assigned as follows [23]:

Peak Name	*Wave number (cm^{-1})*	*Interpretation*
A	2958	ν_{as} CH_3
B	2885	ν_{as} CH_3
C	2838	ν_{as} CH_3
D	1461	δ_{as} CH_2
E	1380	δ_{as} CH_3
F	1165	isotactic bonds
G	997	isotactic bonds
H	977	isotactic bonds
I	843	r_{C-H}
J	1670-1690	ν_s C=O
K	3300-3415	ν_s O-H

It is observed in the IR spectra that the isotactic bands at 1165 cm^{-1}, 997 cm^{-1} and 977 cm^{-1} (3/1 helix) almost disappear with gamma irradiation at the dose of 10^6 Gy, which means the isotactic arrangement of the polymer is no longer present in the polymer matrix.

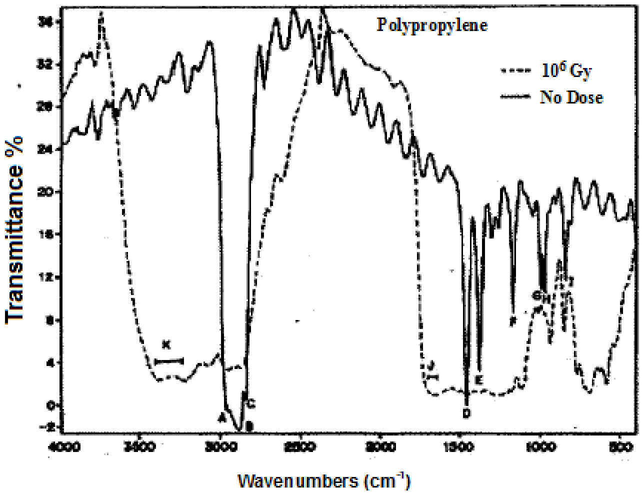
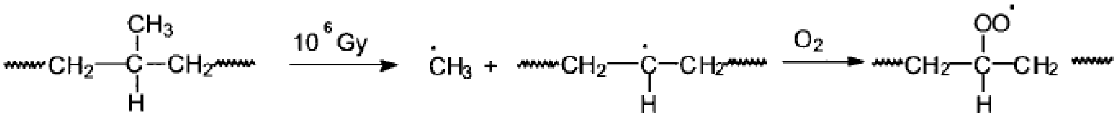


Fig.1. FT-IR spectra of pristine and gamma irradiated Polypropylene

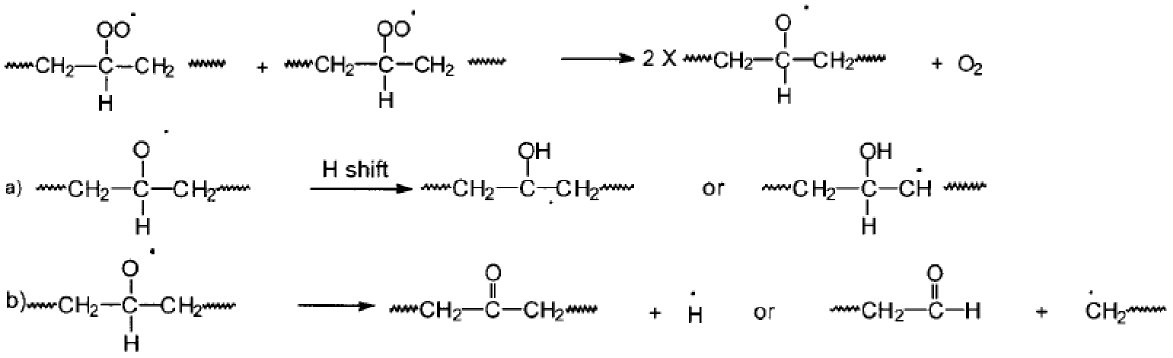
The characteristic peaks of methylene and methyl groups A, B, D and E disappear, indicating the fact that methylene and methyl groups get ruptured at the dose of 10^6 Gy. Interestingly no new sharp peak is observed due to gamma exposure. Only one broad band around 3300cm^{-1} – 3415cm^{-1} appears in the spectra, which is the signature band of alcoholic group (O-H stretching). This indicates that some alcoholic groups are formed in the irradiated polymer. It can be observed in the spectrum of irradiated polypropylene that a slight shoulder develops in the wavelength region 1670 cm^{-1} to 1690 cm^{-1}, probably due to the formation of some C=O groups.

The mechanism for formation of alcoholic or ketonic (C=O) groups is not very clear. Gamma degradation process involves initiation, propagation, and termination stages. The initiation reaction may take place at different sites of the PP chain [1]. When energy is absorbed from gamma rays, it causes scissioning of the covalent backbone. Since it is evidenced that the isotactic arrangements as well as the C-H bond of the methylene group breaks, so out of several preferred initiation routes proposed by Tidjani and Watanabe [1], the most probable mechanism may be as follows:



$$\sim CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2\sim \xrightarrow{10^6\,Gy} \dot{C}H_3 + \sim CH_2-\underset{H}{\dot{C}}-CH_2\sim \xrightarrow{O_2} \sim CH_2-\overset{OO^{\bullet}}{\underset{H}{C}}-CH_2\sim$$

Afterwards propagation occurs by unzipping or by radical abstraction of neighbouring H atom. The result of this is that radical is transferred to another chain or further down the same chain. So the possible mechanism for the formation of alcohol or C=O as proposed by us [23] is as follows:



$$\sim CH_2-\overset{OO^{\bullet}}{\underset{H}{C}}-CH_2\sim + \sim CH_2-\overset{OO^{\bullet}}{\underset{H}{C}}-CH_2\sim \longrightarrow 2\,X \sim CH_2-\overset{O^{\bullet}}{\underset{H}{C}}-CH_2\sim + O_2$$

$$a)\ \sim CH_2-\overset{O^{\bullet}}{\underset{H}{C}}-CH_2\sim \xrightarrow{H\ shift} \sim CH_2-\overset{OH}{\dot{C}}-CH_2\sim \text{ or } \sim CH_2-\overset{OH}{\underset{H}{C}}-\dot{C}H\sim$$

$$b)\ \sim CH_2-\overset{O^{\bullet}}{\underset{H}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{O}{\overset{\|}{C}}-CH_2\sim + \dot{H} \text{ or } \sim CH_2-\overset{O}{\overset{\|}{C}}-H + \dot{C}H_2\sim$$

The FT-IR spectra **polycarbonate polymer**, both pristine (100 µm) and also irradiated at higher doses are shown in figures 2 and 3. It is clear from both the figures that the peak intensities and positions for some of the major bands change drastically due to gamma exposure at doses higher than 10^5Gy. Though neither total destruction nor formation of new peaks take place at the dose of 10^5Gy, the intensities of peaks corresponding to C=O bonds (1725 cm^{-1}), aromatic C–O bonds (1434 cm^{-1}), C-O-C bonds (1206 cm^{-1}), C-H bonds of CH_3 group (2968 cm^{-1} and 2874 cm^{-1}), and aromatic C-H bonds (999 cm^{-1}) decreases. This indicates that scissioning of these bonds take place at this dose. When the dose becomes as high as 10^6Gy, the changes become very apparent. At this dose, most of the major peaks almost disappear (Fig. 3) and a strong peak appears at 1063 cm^{-1}. The carbonyl peak shifts from 1725 to 1599 cm^{-1}. This shift towards lower frequency of carbonyl bond is probably due to the decrease of the C=O bond order.

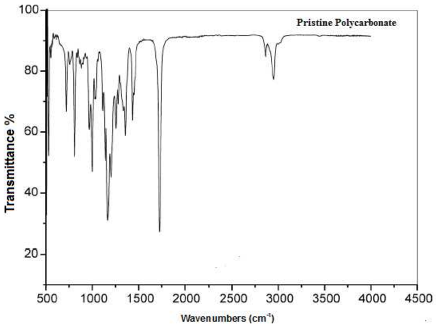


Fig. 2. FT-IR spectra of pristine polycarbonate polymer

Because of irradiation, scissioning of chains take place and as a result, the free radical density or in other words the electron density in the polymer matrix increases. This increase in electron density is responsible for the decrease of the C=O bond order which subsequently lowers the absorption due to the carbonyl groups. Again, one can see that a broad band appears around 3500 cm^{-1}.

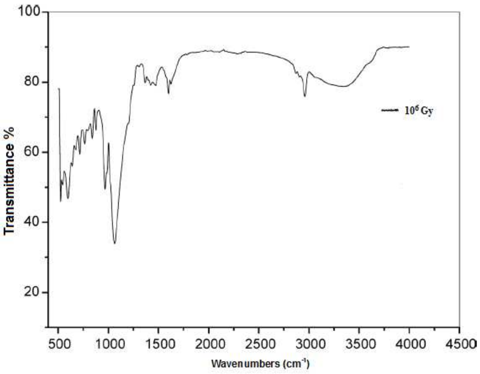
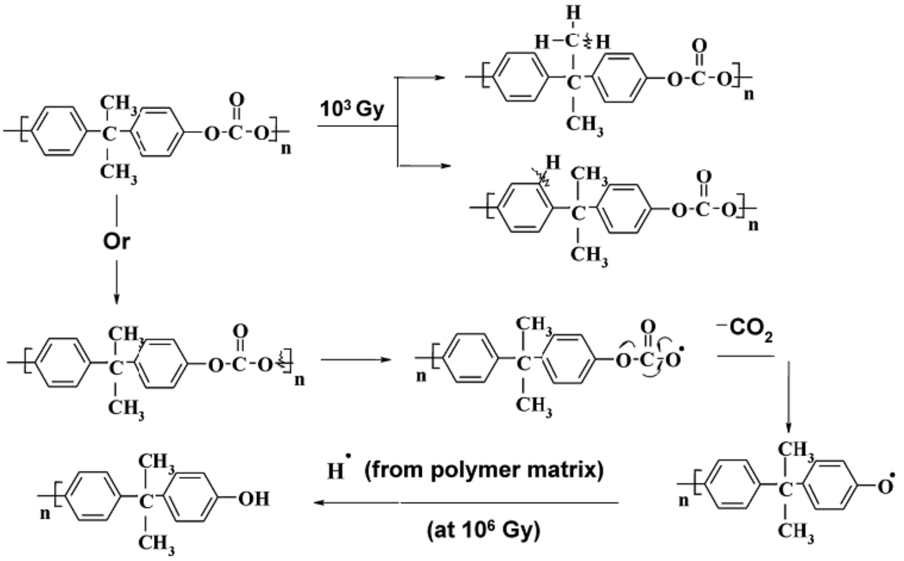


Fig. 3. FT-IR spectra of gamma-irradiated polycarbonate at the dose of 10^6 Gy

This broad band is due to the formation of phenolic groups (-OH groups). It is evident from the IR spectrum of the polymer irradiated with 10^6 Gy that due to gamma exposure, the ester linkages break and probably ester radicals are formed (see mechanism), thus leading to the formation of oxygen radicals. The oxygen radicals once formed can easily pick up hydrogen radicals (which are formed due to cleavage of C -H bonds) and form phenolic groups. In an effort to explain the chemical changes that take place, a probable mechanism has already been proposed [24]:



FT-IR study of **Triafol-BN** also gives some information about its structural changes. In some of the relevant regions like the 1600 to1800 cm^{-1} (ester carbonyl region) and the 2850 to 3000 cm^{-1} (C-H stretching region), the absorbance decreases due to gamma exposure at the highest dose. The peak position at around 2360 cm^{-1}, which is due to the presence of CO_2, also becomes very intense at 10^6 Gy. This is possible if some of the ester groups of the detector are destroyed by radiation and produce CO_2 which, in turn, remains trapped in the detector matrix [21] as is indicated by the spectra:

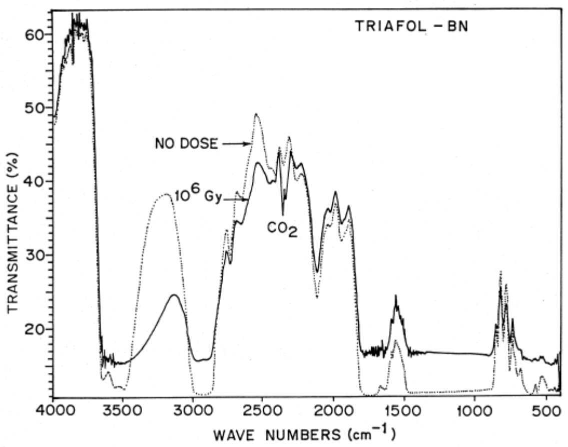


Fig.4. FT-IR spectra of pristine and gamma irradiated (10^6 Gy) Triafol-BN [21]

For **PADC polymeric detectors**, there is no apparent change in the IR spectra due to gamma exposure (Figure 5). Moreover, due large thickness of PADC detectors, the IR spectra goes below the base line, so the changes do not become apparent, even though it was observed from some other studies that the bonds joining polyalyl chains with diethylene glycol could have been ruptured forming radicals [27]

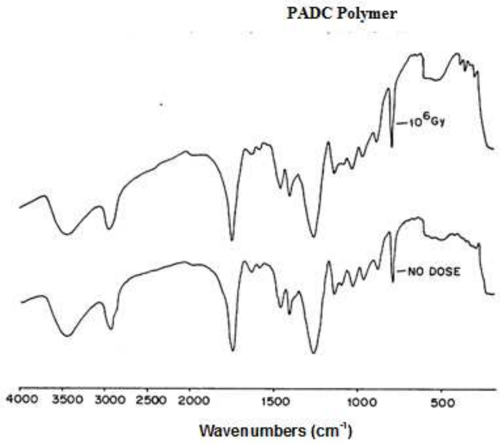


Fig.5. FT-IR spectra of pristine and gamma irradiated (10^6 Gy) PADC (American Acrylics)[27]

CONCLUSION

On the results of FT-IR spectroscopy, it is concluded that due gamma exposure structural modifications of polymeric materials takes place and this modifications are significant mostly at the highest dose of 10^6 Gy. Given below are the conclusions that have been deduced from this work:

1. Random destruction of the polypropylene polymeric chain takes place with the probable formation of alcoholic and ketonic groups
2. For Polyvinyl Chloride polymer, at the dose of 10^6 Gy, observable scissioning of the C-Cl bonds takes place leads to formation of double bonds in the matrix
3. Owing to gamma exposure, polycarbonate polymer forms phenolic group at the dose of 10^6 Gy. This phenolic group forms due to cleavage of ester bonds.
4. For PADC polymeric detectors, there is no apparent change in the IR spectra due to gamma exposure.
5. The ester groups of the Triafol-BN film detector are destroyed by gamma radiation and produce CO_2 at the dose of 10^6 Gy.

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