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Gamma irradiation-based structural property

tailoring of PVC and its electrical behaviour

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ABSTRACT: This article reports on the exposure of polyvinyl chloride to gamma irradiation at various dosages in order to tune its structural properties. The electrical characteristics of the structurally modified PVC are highlighted. Gamma doses ranging from 0 to 50 Mrad were applied to the polymer. Before and after each phase of the process, the polymer was characterised using XRD, FTIR, and crystal size analyses. The electrical properties of the polymer, such as DC conductivity, AC conductivity, and capacitance, were investigated before and after gamma irradiation. XRD analysis reveals that increasing the dosage of gamma irradiation causes the samples to become more crystalline. The electrical property increases in relation to the dosage to which PVC was exposed. The obtained results show that the DC conductivity was 1.79E-8 Ω -1m-1 at 0Mrad and increased to 2.02E-7 Ω -1m-1as the dosage was increased to 50Mrad.

KEYWORDS: - XRD, FTIR, Gamma irradiation, DC conductivity, AC conductivity, capacitance.

I. INTRODUCTION

The infinite advancement of polymer science and the widespread use of polymeric materials in all fields of technology have led to an increase in interest in the various problems of polymer physics and chemistry in recent years. One of the primary goals of polymer physics is to understand the relationship between the chemical and physical structure of polymers and their physical properties. Exposure to ionising radiation has several uses in the fields of industry, medicine, education, research centres, and nuclear facilities [1]. Ionizing radiation, such as gamma rays, causes changes in the physicochemical properties of a polymer [2]. In particular, chain scission, which reduces crosslinking and molar mass, which raises molar mass and decreases solubility, are observed in polymeric materials exposed to gamma radiation [3]. The most frequently produced synthetic plastic polymer worldwide is polyvinyl chloride (PVC) [4]. PVC, or poly (vinyl chloride), has a polyhalogenated strand with chlorine atoms covalently attached to carbon atoms. As a result, the polymer has many points of dipolar interaction along its chain, leading to strong interchain interactions and the material's resulting stiffness [5]. Gamma radiation causes the PVC, to change in terms of its physicochemical characteristics [6]. The thermoplastic polymer polyvinyl chloride (PVC) is non-flammable, light, strong, and incredibly long-lasting. It has several uses in the industrial sector, in automobiles, in medical research, and in food packaging [7]. Insulation made of irradiated PVC offers various advantages. It will endure significantly greater temperatures than typical PVC insulation, and insulation subjected to radiation may make insulation more resistant to heat, abrasion, and cutting than ordinary insulation [8]. It is well known that energetic gamma rays harm the molecular makeup of polymers. The majority of research on these radiation impacts has focused on the overt consequences visible in the change in dc conductivity [9]. Here, we've tried to change PVC's structural characteristics by subjecting it to gamma radiation at various intensities. Characterising features of the PVC and modified PVC were analysed with cutting-edge methods, and the electrical characteristics of these material were examined.

II. EXPERIMENTAL

Commercially available PVC samples (PVC samples that were received from POLYPENCO Ltd (UK)) were cut into disc shapes with a 6 mm radius and 1.1 mm thickness for the current study. At CTRL (Cotton Textile Research



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Laboratory), Mumbai, these discs were exposed to Co60 radiation at a dose rate of 0.25 Mrad/hr while being in the presence of air. The dosages of radiation used to treat the PVC samples included 0, 10, 20, 30, 40, and 50 Mrad.

III. CHARACTERIZATION

The resultant product was subjected to X-ray diffraction tests at room temperature using a RIGAKU Miniflex II Series X-ray diffractometer and a CuK radiation. Following that, KBr was combined with powder samples of unirradiated and irradiated polymer samples, and the pallet was ready. The sample is made by completely combining KBr and the substance whose FTIR readings will be recorded in the ratio of 100:3. A FT-IR, JASCO 460 Plus spectra photometer was used to record the FTIR spectra for those pallets in the wave number range of 4000 cm-1 to 400 cm-1. The electrical conductivity of the unirradiated and irradiated samples were carried using the two probe method with the help of Keithly electrometer model 2400, at room temperature. The capacitance ,Loss factor and A.C. Electrical conductivity in the frequency range of 10 kHz to 150 kHz of the unirradiated and irradiated polymer samples were recorded using the LCR bridge interfaced in the frequency range 10K to 2M with the help of Impedance Analyzer (HP 4192A) and HP 4275A multi frequency at room temperature.

IV. RESULT AND DISCUSSION

XRD Studies



Fig.1. XRD pattern of non-irradiated and irradiated PVC

Fig.1 depicts the X-ray diffraction pattern for unirradiated and irradiated PVC samples. Unirradiated PVC (0 Mrad) XRD pattern reveals the material's amorphous nature. The PVC sample's partially crystallinity or amorphous nature has been noted. When the material was subjected to gamma radiation at a dose of 10Mrad, the emergence of new Bragg's reflection was seen. This demonstrates how crystalline nature gradually develops from amorphous nature when exposed to radiation. However, the XRD reveals the development of more pronounced peaks when the PVC sample was exposed to radiation at a 50Mrad intensity. This demonstrates how samples crystallise more as gamma radiation dose is increased. This research allows us to draw the conclusion that the amorphous nature of the material transforms into crystalline as the dosage of gamma radiation increases. These findings demonstrate unequivocally that the irradiation did not damage the initial crystal lattice and that the technique increased crystallinity overall. The XRD pattern makes it very evident that the irradiation had no effect on the peak locations. The alignment of tiny chain polymer fragments created by irradiation may be the cause of the rise in crystallinity. This research allows us to draw the conclusion that the sample's crystallinity increases as the irradiation dose rises, demonstrating the improvement in crystallinity [10, 11].

Crystal size analysis

Crystal size analysis was carried out to know the change in the grain size of the material on exposure to the gamma radiation at different dosage level. The crystal size of the material was calculated using Scherrers's method [12]. The result obtained is given in the Table 1. From the Fig 2 we conclude that the size of the crystal increases with respect to an increase in the dosage of gamma irradiation. It was observed that the size of the crystal was 4.95438E-11meter when



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exposed to 0 Mrad whereas the dosage increases from 0 to 50 Mrad the size of the crystals has increased from 4.95438E-11 to 8.69457E-11meter respectively.



Fig.2. a) Radiation doses verses crystalline and amorphous nature of gamma irradiated PVC, b) Variation of crystal size verses dosage of gamma irradiation on PVC

Table 1. Variation of crystal size of PVC verses different dosage of gamma irradiation

| Dosage of gamma | Full width half maxima of | Crystal size (10-9) |
|-------------------|---------------------------|---------------------|
| radiation in Mrad | crystalline peak | meter |
| 0 | 2.867 | 0.0495 |
| 10 | 1.662 | 0.0854 |
| 20 | 1.654 | 0.0858 |
| 30 | 1.653 | 0.0859 |
| 40 | 1.642 | 0.0865 |
| 50 | 1.633 | 0.0869 |

FT-IR studies



Fig.3. FT-IR pattern for irradiated and unirradiated PVC

The change in chemical structure of PVC due to gamma irradiation is identified by FTIR spectroscopy. Different modes of vibration in the sample was observed as given in Table 2. The following is an examination of the FTIR spectra of PVC that has been exposed to radiation. Peaks at 680 cm-1 in the case of the unirradiated PVC sample indicate that the chlorine atom is bonded to the carbon and that this region has a strong absorption, or C-Cl stretching mode of vibration. The C-Cl stretching overtone peak is at 1338.53 cm-1, while the C-C stretching vibration peak is at



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2360.75 cm-1; both have strong absorption regions. The middle absorption region's peak at 1434 cm-1 represents the C-H bending mode. The medium absorption zone at 2916.2 cm-1 indicates the C-H stretching mode of vibration. For the PVC50 sample that was exposed to radiation, the FT-IR spectra show peaks at 617.19 cm-1, which represent the chlorine atom bound to carbon. i.e., the C-Cl bond weakens as a result of the radiation. The chlorine atom breaks free. The carbon atom bound to the hydrogen atom and the carbon atom bound to the chlorine atom breaks free. The carbon atom bound to the hydrogen atom and the carbon atom bound to the chlorine atom are double bonded. This is brought on by possible chlorine liberation or a weakening of the C-Cl bond. The peak for this double bond was 1602.76 cm-1. The 2916.2cm-1 peak, which indicates C-H stretching, is broad and in the region of medium absorption. The peak at 2360.7cm-1, which is unaffected by irradiation, is C-C stretching. Following irradiation, the polymer samples' total transmission intensity falls, which suggests that the materials' structural integrity may have been disturbed. After irradiation, the C-Cl stretch intensity at 625 cm-1 dramatically drops. [13-15].

| Table 2. Different modes of vibration in the sample | e as observed from FTIR data |
|---|------------------------------|
|---|------------------------------|

| Mode of vibration | Unirradiated sample | Irradiated sample | Wave number (cm-1) |
|---------------------------|---------------------|-------------------|--------------------------|
| C-Cl stretching vibration | Present | Present | 680 |
| C-Cl stretching overtone | Present | Present | 1338 |
| C=C stretching vibration | Absent | Present | 1680 |
| C°C stretching vibration | Present | Present | 2360 |
| C-H plan bending mode | Present | Absent | 1434 |
| C-H asymmetry stretch | Present | Present | 2916 |
| C-H stretching | Absent | Present | 3448 |

Analysis of Zero pint energy and force constant

The analysis of Zero pint energy and force constant for FT-IR spectra of unirradiated and irradiated PVC samples are given in Table 3. The zero point energy of the unirradiated PVC is 0.3127eV and after the irradiated due to PVC sample are gradually decreasing from 0.3011eV to 0.2984eV for 10Mrad to 50Mrad respectively. The force constant found unirradiated PVC sample is 427.10 Nm-1 and after the irradiation due to the PVC sample are found drastically decreasing from 347.74 Nm-1 to 319.23 Nm-1 for 10Mrad to 50Mrad in the following table 2. By these studies we can say that by increasing the dosage, the stiffness of the polymer reduces. The zero point energy ($\lfloor 0$) and force constant (K) calculated by using formulas follows [16, 17].

$$\epsilon_{0} = \frac{1}{2}hc\sum_{i=1}^{4}U_i$$
 and $K = 4\pi^2\mu c^2\overline{U}_e^2$

| Polymer | Zero-point | Force Constant |
|----------|-------------------|----------------|
| sample | Energy $(e_o) eV$ | (K) Nm-1 |
| 0 M rad | 0.3127 | 427.104 |
| 10 M rad | 0.3011 | 347.741 |
| 20 M rad | 0.3004 | 341.942 |
| 30 M rad | 0.2994 | 334.966 |
| 40 M rad | 0.2989 | 324.435 |

Table 3. Zero point energy and Force constant as observed from FTIR data

Electrical Properties of PVC

DC conductivity studies

Fig. 4 shows the DC electrical conductivity of the treated PVC at room temperature under various gamma radiation dosages. The outcomes are presented in Table 4. The graph clearly shows that the conductivity of the material increases



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as the radiation exposure does. According to the data, the conductivity was $1.79E-8 \Omega - 1m-1$ at 0Mrad and increased to $2.02E-7 \Omega - 1m-1$ at 50Mrad when the dosage was increased. Additionally, it was shown that conductivity grows steadily up to 40 Mrad before rapidly increasing beyond that. This might be caused by a greater quantity of polymer chain breakdown, which is linked to the generation of free radicals. The electrical conductivity increases as the irradiation dosage increases because more ions are generated [18, 19].

| Radiation(M | Resistivity | Conductivity(Ω- |
|-------------|--------------|-----------------|
| rad) | (Ωm) | 1 m-1) |
| 0 | 5.6E+07 | 1.79E-08 |
| 10 | 4.8E+07 | 2.07E-08 |
| 20 | 3.2E+07 | 3.13E-08 |
| 30 | 8960782 | 1.12E-07 |
| 40 | 6263154 | 1.60E-07 |
| 50 | 4958115 | 2.02E-07 |

Table 4. DC Electrical conductivity of gamma irradiated PVC at room temperature



Fig.4. DC Electrical Conductivity v/s Dosage of gamma irradiation on PVC

Capacitance Studies

In Fig. 5, it is shown how the capacitance of PVC samples changes with increasing frequency and varied gamma radiation dosages. The figure clearly shows that the material's capacitance increases with an increase in gamma radiation exposure. Furthermore, it has been found that the material's capacitance reduces as frequency rises. The graph indicates that the capacitance of the material in each case abruptly decreases up to a frequency of 40 kHz and then progressively decreases as the frequency rises. As the frequency rises, the charge carriers move through the dielectric and become trapped against a defect sight, where they generate an opposing charge. Because polarisation of trapped and bound charges is impossible at these frequencies, and hence, the dielectric constant falls. [20].



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Fig 5. Variation of capacitance v/s Frequency with constant dosage of gamma irradiation AC conductivity Studies

The ac conductivity (σ ac) was obtained from the data of dielectric constant (C') and loss tangent (tan δ) using the relation

 $\sigma ac = \omega \in C' \in O \tan \delta$

Where, C0 is the permittivity of free space

 ω is the angular frequency = 2 Π f

The variation of σac with frequency is as shown in the Fig.6 for all samples. The graph displays the relationship between the conductivity of a PVC sample and frequency for both irradiated and unirradiated samples at room temperature. The conductivity was found to gradually increase as the frequency rose. Additionally, it has been found that the AC conductivity increases as gamma radiation exposure increases. The scissioning of polymer chains that causes the rise in conductivity after irradiation may be responsible for the increase in free radicals, unsaturation, and high enough AC fields that may result in a net polarisation that is out of phase with the field. This finding indicated that conductivity rose at higher frequencies [21].



Fig. 6. Variation of AC conductivity verses frequency at different dosage of gamma irradiation

V. CONCLUSION

According to our research, gamma irradiation can be a useful tool for modifying the structural characteristics of PVC. According to XRD tests, the percentage of crystallinity increases as the dosage of gamma irradiation increases. Force constant investigations show that the toughness of the polymer decreases as the crystallinity rises, indicating the creation of pores and voids inside the polymer. According to conductivity tests, exposure to gamma radiation causes the polymer's internal connections to break, which results in the creation of free radicals. Electrical investigations show that these free radicals travel freely via pores, gaps, and channels within the polymer when charge is applied. According to the aforementioned investigations, it can be concluded that these PVC can be employed in active electrode components as energy storage, electrochemical sensors, as well as conversion sectors including supercapacitors, solar cells, fuel cells, and lithium-ion batteries.



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