Influence of gamma radiation on PVC/PANI composites

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Abstract. PVC/PANI composites radiated with 75Kgy of Gamma radiations were studied for their modifications in optical and structural properties as compared to the pristine polymer composites. The study of FTIR spectra of gamma radiated and pristine samples of polymer composite shows that the intensity of peaks decreases with gamma irradiation and at the same time shifts towards lower wave-number for pure PVC and its composites. It is further found that the water content has been reduced with Gamma irradiation and CO2 was released. The UV-VIS spectra for PVC/PANI composites were studied after irradiation with 75Kgy of Gamma radiation and compared with the pristine composites. It was observed that the direct band gap, indirect band gap and urbach’s energy increases with gamma irradiation for pure PVC which may be attributed to increased cross linking in PVC due to irradiation. For other concentrations of PANI in composite the direct band gap, indirect band gap and urbach’s energy is found to decrease with irradiation. PL studies of composite showed that with the addition of PANI the colour of emission has been found to shift towards yellow. After irradiation the emission colour has been found to shift towards white colour where as negligible effect has been found for composites with higher concentration of PANI.

1. Introduction-
Conductive polymers due to the spatially extended conjugated π - bonding system and cation radicals in their structures exhibit unique physical, chemical and electronic properties which make them attractive as active components of ‘plastic electronics’, such as polymer light-emitting diodes, field effect transistors, sensors, etc [1,2]. However, Polyaniline (PANI) is considered as one of the most promising electrically conducting polymer due to its ease of synthesis and low production cost, light weight [3], excellent environmental stability and oxidation resistance [4], good photo-electricity, high heat resistance and good electrical conductivity, good electro-chromic effects and unique reversible acid base chemistry [5-9] Conducting polymers especially PANI is obtained in powdered form. The insolubility, infusibility and poor processibility of the polymer limit their practical applications. Different methods have been adopted to overcome these limitations. However, blending the polymer with other polymers in a co-solvent [10], combine electrical properties of PANI and high mechanical strength of conventional polymer thus enhancing the commercial viability of these blends [10]. The interaction of ionizing radiation with matter can significantly modify the molecular structure of the irradiated material. Properties of the materials can be modified by varying different irradiation parameters like Irradiation dose, Irradiation dose rate, temperature, pressure etc. Studies have been devoted to understanding the mechanisms of the modification of the molecular structures and of the
properties of polymers resulting from exposure to ionizing radiation. Radiation treatment of polymers can be used to investigate crystal morphology, reinforcement, and electrical properties.

2. Experimental

PANI was obtained by oxidative polymerization of aniline hydrochloride using ammonium peroxy disulphate as oxidizing agent. 0.2M solution of aniline hydrochloride and 0.25M solution of ammonium peroxydisulphate in distilled water were mixed together and left undisturbed for a minimum of 24 hrs. The precipitates were then filtered, washed dried overnight at a constant temperature of 70°C. PVC/PANI composites with varying concentration of PANI between 0 to 50% were synthesized by solution blending method using Dimethyl acetamide (DMac) as a solvent. The composites were then irradiated with 75KGy of gamma radiation at a dose rate of 3.383 kGy/h in Vacuum from Gamma Chamber 1200 at IUAC New Delhi. The variation of direct and indirect band gaps between conduction and valence band for all PVC/PANI composites after irradiation have been calculated from the Ultraviolet-Visible (UV-VIS) spectra taken in the wavelength range of 200-900 nm using UV-2600, Shimadzu, Japan spectrophotometer and compared with that of un-radiated composites. The photoluminescence properties of PANI/PVC blends with varying PANI Concentration and irradiation with 75KGy of gamma radiation have been analyzed in the range of 420-600 nm at an excitation potential of 405 nm using the Perkins Elmer LS55 fluorescence spectrophotometer. Infrared spectra of the composites to study the variations in the vibrations modes of the groups/ radicals have been analyzed in the spectral range of 4000-400 cm⁻¹ using the Shimadzu FTIR-8400S.

3. Results and discussion

The results obtained from various observations have been analyzed and the outcomes have been discussed on the basis of conformational and structural modifications in the blends and the findings have been discussed below.

3.1 Structural analysis

The FTIR analysis of PVC/PANI composites before and after irradiation has been performed and the results are shown in figure1 and figure 2 respectively. The peak at 3432 cm⁻¹ of pure PVC has been found to diminish with irradiation while the peak is completely eliminated with addition of polyaniline. A peak at 2971cm⁻¹ corresponding to aromatic C-H stretching has been found to decrease in intensity, with irradiation. A peak at 2913 cm⁻¹ corresponding to asymmetric C-H stretching of PVC is found to decrease in intensity with irradiation. A peak at 2845 cm⁻¹ corresponding to symmetric C -H stretching of PVC has been found to decrease in intensity with irradiation. A peak at 2358 cm⁻¹ corresponding to the presence of CO₂ has been found to shift towards higher wave number and at the same time shows increase in intensity with irradiation. The peaks at 1550 cm⁻¹, 1499 cm⁻¹, 1392 cm⁻¹ and 1349 cm⁻¹ have been found to be lost with addition of polyaniline. Two new at peaks 1578 cm⁻¹ and 1504 cm⁻¹ have appeared with addition of polyaniline and have been found to increase in intensity with irradiation. A peak at 1644 cm⁻¹ has found to decrease in intensity with irradiation. The intensity of the peak at 1254 cm⁻¹ has been found to increase with gamma irradiation and has been shifted towards higher wave number with addition of polyaniline The peak at 1192 cm⁻¹ found to shift towards higher wave number and corresponds to C-C stretching vibrations. This may be due to interaction between N=Q=N bending in polaron.
3.2 UV-Vis analysis

UV-Vis absorption spectra of the PANI/PVC composites for different PANI concentration have been studied before and after irradiation with 75Kgy of Gamma radiation to study effect of radiation on the composites. The results have been shown in figure 3 and figure 4.
The shift of absorption edge towards longer wavelength indicates reduction in chain length due to increased interaction between PVC and PANI molecules that reduces the band gap with increase in PANI Concentration as well as irradiation. Wide bands are observed in composites with 10% and 20% concentration of PANI due to formation of colour centers, which diminishes for higher concentration due to higher interaction between PVC and PANI molecules. With irradiation the bands have been found to shift towards higher wavelength. Moreover direct and indirect band gap have been calculated from absorption spectra by using Tauc’s formula [11] and have been reported in table 1. It has been observed from the table that the indirect band gap is always greater than direct band. This shows that the PVC/PANI composites can be used for direct band gap applications, because it would require extra energy for photon interaction as compared to direct band gap which would be wastage of energy. It has been further observed that both the direct and indirect band gap energies reduce with increase in concentration of PANI in the composites. The reduction in band gap may be attributed to the increasing interaction between PVC and PANI moieties with increase in concentration. The Urbach’s energy [12] has been found to increase with increase in PANI concentration as well as with irradiation. The increase in tailing with concentration of PANI may be due to increased charge storage in the form of impurities and formation of polarons and bi-polarons. Moreover the tailing has been found to reduce with irradiation.

Table 1: Variation in direct, indirect and Urbach’s energy with the increased concentration of PANI in PVC/PANI blends

| Concentration of PANI in PVC/ PANI blends (%) | Direct Band Gap (eV) | Indirect Band Gap (eV) | Urbach’s Energy (eV) |
|-----------------------------------------------|----------------------|------------------------|----------------------|
|                                               | unirradiated | irradiated | unirradiated | irradiated | unirradiated | irradiated |
| 0                                             | 5.22        | 4.70       | 5.74        | 5.53       | 0.09        | 0.92       |
| 10                                            | 2.42        | 2.56       | 2.76        | 3.99       | 0.18        | 0.61       |
| 20                                            | 2.28        | 1.91       | 2.70        | 2.71       | 0.26        | 0.56       |
| 30                                            | 2.10        | 1.36       | 2.65        | 2.45       | 0.35        | 0.97       |
| 40                                            | 1.64        | 1.37       | 2.49        | 2.47       | 0.73        | 0.98       |
| 50                                            | 1.16        | 1.30       | 2.40        | 2.51       | 0.99        | 0.94       |

3.3 Photo-luminescence

The photoluminescence spectra of PVC/PANI composites have been measured at an Excitation of 320nm with and without irradiation and the results have been shown in figure 5 and figure 6.
It has been found that the photoluminescence intensity of pure PVC is highest. The photoluminescence intensity of the composites increases monotonically with the increase in PANI concentration but is always less than that of pure PVC. The photoluminescence of the blends were calibrated for D65 illuminant and the CIE 1931 X,Y,Z Co-ordinates have been calculated and reported in table 2 and table 3 along the corresponding tristimulus chromaticities depicted from the CIE chromaticity diagram figure 7 and figure 8. The application of fluorescence spectroscopy of conjugated polymers has been found to be useful to study photo physical processes of these polymers in the electrochemical environment [13] due to Keir utilization in OLED and OPV. The main reason behind the red shift may be the conformational disorder and the exciton quenching by polarons due to Forster resonance energy transfer or charge transfer mechanisms [14]. The interactions of PVC and PANI side chains or main chains lead to the variation and efficiency of luminescence and their temporal evolution.

Table 2: Variation of CIE coordinates, Tristimuluschromaticities and the wavelength corresponding to CIE coordinates with the increased concentration of Pani in PANI/PVC blends

| S.No. | Percentage of PANI | CIE Coefficients | Tristimuluschromaticities |
|-------|-------------------|------------------|--------------------------|
|       |                   | X    | Y    | Z     | R    | G    | B     |
| 1     | 0                  | 0.379 | 0.425 | 0.197 | 188.835 | 173.585 | 116.839 |
| 2     | 10                 | 0.395 | 0.44  | 0.165 | 196.397 | 175.839 | 107.651 |
| 3     | 20                 | 0.408 | 0.452 | 0.139 | 196.950 | 180.329 | 78.627 |
| 4     | 30                 | 0.421 | 0.466 | 0.113 | 202.148 | 182.535 | 61.765 |
| 5     | 40                 | 0.422 | 0.469 | 0.110 | 202.167 | 183.322 | 59.245 |
| 6     | 50                 | 0.432 | 0.470 | 0.098 | 207.678 | 181.876 | 49.881 |
Table 3: Variation in CIE coordinates and Tristimulus chromaticities (RGB colour contents) after gamma irradiation at a dose of 75 KGy of PANI / PVC Composites

| S.No. | PANI Concentration in PVC | CIE Coefficients | Tristimulus chromaticities |
|-------|---------------------------|-----------------|---------------------------|
|       |                           | X    | Y    | Z    | R    | G    | B    |
| 1     | 0                         | 0.32 | 0.37 | 0.31 | 155.47 | 163.85 | 14386 |
| 2     | 10%                       | 0.36 | 0.40 | 0.24 | 176.31 | 167.01 | 127.79 |
| 3     | 20%                       | 0.41 | 0.45 | 0.14 | 198.15 | 173.85 | 99.31  |
| 4     | 30%                       | 0.41 | 0.46 | 0.13 | 197.62 | 176.21 | 95.88  |
| 5     | 40%                       | 0.42 | 0.45 | 0.13 | 202.69 | 172.82 | 95.92  |
| 6     | 50%                       | 0.42 | 0.46 | 0.12 | 202.18 | 175.19 | 92.33  |

4. Conclusion

The transformation of polyaniline from benzenoid to quinoid structure indicated in UV-Vis spectrum of the composites has also been confirmed from the FTIR spectrum. Due to irradiation single wavelength has shifted towards white colour.
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