CHAPTER - 8

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Summary and Scope for
Future Work
Polymers, also known as macromolecules are built up of a large number of molecular units that are linked together by covalent bonds. Polymeric materials are suitable for scientific and technological applications, such as in optical devices, electronics, particle detectors, automotive industry, sterilization irradiators and dosimeters, and space applications. These materials offer unique properties, application prospects and diversity which cannot be matched by any other class of materials. This increased importance of polymers arose out from their advantages such as lightweight, low density, easy processability, high strength-to-weight ratios, low thermal expansion coefficients and low manufacturing costs etc.

Over the last few years, the development of new polymeric materials have been oriented towards doped polymers, polymer blends, polymer composites and irradiation of polymers with high energy ionizing radiation. These systems are more attractive with great significance for research and industrial applications. The main reason to develop these compounds is to obtain a material with specific properties and characteristics and low manufacturing costs. Polymers can be doped with suitable dopants like inorganic salts, neutral molecules or compounds and reducing agents, which can easily form ions. It is also known that the physical and chemical properties needed for a specific application can be tuned by adding or doping with a dopant. Here the interaction of the dopant with polymer matrix plays an important role between functional groups of the polymer and the dopant. On the other hand, polymer blends are being studied these days because of the possible improvement in the physical properties of the mixture incorporating the individual properties of polymers. A polymer blend is a member of a class of materials analogous to metal alloys in which two or more different polymers or copolymers are mixed together to create a new material. Doping of the prepared blend with a transition metal chloride or a chalcone chromophore is also a method towards the synthesis of new polymeric materials with enhanced properties for particular applications.
Recently, ionizing radiation is widely used in the modification of polymeric materials. Hence there has been a special interest in the study of radiation-induced modification of polymers due to their increasing use in radiation environments, viz. nuclear power plants, spacecraft, high-energy particle accelerators, etc. Moreover, the applications of irradiation in polymer technology are of great importance with a view to achieve some desired improvements in polymer properties. The irradiation effects induced by electrons, heavy ions, protons, UV-rays, and gamma rays have been used largely to modify the physical and chemical properties of polymers. The main effects of the interaction of such ionizing radiations with polymers are to produce excitation and ionization of the atoms and molecules in the polymers.

Some of the noticeable changes induced by radiation are scissioning of the polymer chains, 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. All these processes affect the macroscopic properties of the modified polymers, such as mechanical strength, color, electrical conductivity, etc. These radiation induced modifications can be traced back to know the possible microstructural changes that are taking place within the polymeric matrix. Though high dose irradiation destroys the original polymeric structure quite efficiently, it also leads to the formation of the radiation defects (radicals, excess internal free volume) that act as traps for diffusing polymeric decomposition products, thus preventing their escape from the matrix. Furthermore, depending on the chemistry of the polymer, cross-linking might take place during irradiation and it helps in stabilizing the remaining structure. It is reported that the electron beam irradiation causes only chain scission or cross-linking in some cases and both cross-link as well as chain scission in some other cases. The extent of irradiation effect depends on various parameters including chemical structure, morphology of the polymer and irradiation conditions.
In view of this, it is very important to note that the irradiation modifies the microstructure of the polymer. Since the change in polymer properties are mainly depends on the type of irradiation, nature of the polymer (dopant) and its interaction with the polymer matrix, the present investigation aims to understand the effect of 8MeV electron beam irradiation on commercially available polymer such as

(1) Poly(vinyl alcohol) PVA
(2) PVA doped with KCl (monovalent transition metal chloride)
(3) PVA doped with BaCl₂ (divalent transition metal chloride)
(4) PVA doped with FeCl₃ (trivalent transition metal chloride)

In addition, the blend of polymer PVA and PVP (Poly(vinylpyrrolidone) has also been prepared. To know the modifications in the microstructural properties of this blend, it has been doped with FeCl₃ (trivalent transition metal chloride). The PVA/PVP blend has also been doped with a Non linear optically active chalcone chromophore 1-(4-methylphenyl)-3-(4-N, N, dimethyl amino phenyl)-2-propen-1-one (MPDMAPP).

The modifications occurring within the polymer due to electron irradiation and the induced microstructural changes in doped blend/composites are studied by different experimental techniques. The free volume related microstructural changes are studied using Positron Annihilation Lifetime Spectroscopy (PALS) complemented with Wide Angle X-ray Diffraction (WAXD). The modified optical properties are studied using FTIR and UV-Visible spectroscopy and Steady State Fluorescence Spectroscopy. The thermal properties are studied using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). All these extensive studies are presented in seven chapters of this thesis.

The chapter 1 explains a broad outline of the subject including motivation to the present work. It starts with a brief introduction to the polymers, doping of polymers, polymer blends and effect of electron irradiation, purpose of characterization, motivation and aims and objective,
basic idea about techniques used like positron annihilation spectroscopy and other techniques. Chapter 2 gives the experimental details like sample preparation, doping of polymers, preparation of the blend, description of the 8MeV electron accelerator (Microtron), techniques particularly positron lifetime spectrometer, its optimization, the source preparation, data collection and analysis etc. Chapter 3 gives the studies on structure-property behaviour of 8MeV electron beam irradiated PVA. Chapter 4 contains the detailed study of effect of electron irradiation on KCl doped PVA. Chapter 5 contains the study on the microstructure of electron irradiated BaCl₂ doped PVA. Chapter 6 contains the study on the microstructure of electron irradiated FeCl₃ doped PVA. Chapter 7 provides the study on PVA-PVP blend doped with FeCl₃ and NLO active chromophore (MPDMAPP). Each chapter starts with a brief introduction followed by results and discussion as well as a summary of the investigations. A brief abstract of the present investigated results are given below.

**FTIR Studies:**

The FTIR spectroscopic studies on PVA have been carried out to know the modifications in the functional groups due to electron irradiation. No color change was observed in the irradiated pure PVA. But the FTIR spectrum shows changes in the position, shape and intensity of the absorption bands which are sensitive indicators of changes in macromolecular structure. It is found that the electron beam irradiation accelerates the reaction in the O-H group of PVA leading to cleavage of both C-H and O-H bonds. We observe a marked reduction in the intensities of O-H, C-H and C-O bands which further confirms degradation or chain scission (degradation) in the polymer.

In the case of both electron irradiated KCl and BaCl₂ doped PVA, the unirradiated films had white colour as a result of processing and after electron irradiation, colour turned to faint yellow indicating that the morphology of the polymer was affected by electron irradiation. In the case of KCl doped PVA at lower doses, two new absorption bands are appeared at the wavenumbers 1713
cm$^{-1}$ and 1257 cm$^{-1}$ respectively and these are the newly created radicals due to the irradiation which is attributed to the induced polymer chain scission, manifests in the form of polymer degradation. At higher doses, a decrease in the intensity of the bands continues to decrease and these changes indicate that major chemical modifications induced in the polymer complex upon irradiation by the process of crosslinking.

In the case of electron irradiated BaCl$_2$ doped PVA, shifting in band positions with variation in intensity was observed along with a formation of new peaks. The O–H stretching vibration peak at 3421 cm$^{-1}$ has shifted to 3435 cm$^{-1}$ and the peaks at 2921, 2860, 1629, 1384 and 1085 cm$^{-1}$ have shifted to 2925, 2858, 1631, 1380 and 1089 cm$^{-1}$, respectively. New peaks start appearing around 1700 cm$^{-1}$ and 1200 cm$^{-1}$. These results are understood by invoking the conformational changes introduced within the polymer due to electron irradiation, which may be considered as an evidence for the onset of degradation of the polymer. The new peaks at 1265 cm$^{-1}$ for 100 and 200 kGy and 1261 cm$^{-1}$ for 300 kGy irradiation are attributed to stretching vibrations of carboxyl group C–O and are vanish for 400 kGy irradiation. After irradiation with high doses, end product contains C=O groups which is attributed to the chemical changes arising from the rearrangement of the ions to form a stable product leading to crosslinking. These study shows that the Chain scission is the main process at the lower doses and at higher doses, cross-linking is dominant.

In the case of electron irradiated FeCl$_3$ doped PVA; slight shifting in band positions with small variation in intensity was observed along with a formation of new peaks. These modifications are attributed to creation of radicals which helps in further crosslinking of the polymer composite.

In the FTIR spectra of PVA+PVP blend doped with FeCl$_3$ and with MPDMAPP, shifting of characteristic band positions and variations in the band intensities are observed. The appearance of new peaks along with changes in existing peaks (and/or their disappearance) is a direct indication of the
complexation with in the blend and formation of radicals with in the composite. This FTIR studies suggest that the chalcone chromophore MPDMAPP is strongly interacting with the PVA+PVP blend.

**UV-Visible Studies:**

The UV-Vis optical absorption studies on unirradiated PVA shows the absorption around 195nm, assigned to $n \rightarrow \pi^*$ transitions and at 275nm assigned to $\pi \rightarrow \pi^*$ transition and transparent in the visible region.

In the case of high energy electron irradiated PVA, KCl doped PVA and BaCl$_2$ doped PVA films the shift in the absorption edge towards the longer wavelength side of the spectrum and increase in absorption with increase in electron dose was observed. For PVA, new absorbance peak appeared at the 275nm assigned to $\pi \rightarrow \pi^*$ transition shifts to 280nm. Due to irradiation, chain scission (degradation) of PVA is observed. In the case of irradiated KCl doped PVA a peak at 200nm (due to $n \rightarrow \pi^*$ transitions) shifts to 211nm for 600kGy and becomes broader upon irradiation. This is due to the formation of conjugated double bond C=C and manifested in the form of increased absorbance and shift of absorption edge towards longer wavelengths. The significant shift in the transition energies and appearance of shoulder is attributed to the formation of unsaturation and crosslinking at higher doses. Thus the increase in absorption peak height, peak centroid shifts, broadening in the peak and shift in the band tail towards longer wavelengths with the increasing irradiation dose suggests the modifications of the optical properties due to irradiation. Thus both KCl and BaCl$_2$ doped PVA films show main chain scission at lower doses and cross-linking at higher doses electron irradiation.

Electron irradiated PVA and KCl doped PVA show the presence of two optical energy gaps which decreases with increasing electron dose. The irradiated BaCl$_2$ doped PVA shows a single optical energy gap, which also decreases with increasing electron dose. The decrease in $E_g$ is attributed to the creation of point defects that exist in the band gap during the irradiation by the interaction of electrons with the lattice atoms and by multiple collisions.
The UV-Vis study on chalcone chromophore MPDMAPP doped PVA/PVP composite films shows three absorption regions with blue shifting, three absorption edges. These absorption results indicate that the MPDMAPP interacts with PVA/PVP matrix via intermolecular hydrogen bonding and hydrophobic interaction and forms the charge transfer complex or charge cluster groups and affect the optical properties.

Fluorescence studies:

The Fluorescence study on chalcone chromophore MPDMAPP doped PVA/PVP composite films shows increase in the fluorescence emission intensities and emission wavelengths indicates that the chalcone molecules in a crystalline state are less fluorescent but strongly fluorescent in the polymeric matrix due to the specific intermolecular interactions. The fluorescence polarization $P$ and anisotropy $r$ for the composite films were measured and these values are low for pure chalcone and these parameters increases for composites films. The fluorescence microscopic images of the composite films show that the composite films are photochromic in nature. Thus doping can effectively modify the macroscopic properties of the blends and they can be tuned for particular applications by controlling the dopant concentration.

XRD studies:

The XRD pattern for the unirradiated PVA indicates that the polymer is semicrystalline in nature. As the electron dose is increased the intensity of the diffraction peaks becomes lesser indicating the increase of amorphous nature of PVA after electron irradiation.

The unirradiated KCl doped PVA film shows a prominent peak at $2\theta = 28.95^\circ$ and a smaller peak at $41.11^\circ$ characterizing the crystalline phase of PVA composite. After irradiation, significant structural changes are observed like an increase in peak intensities with irradiation dose which shows that the crystallinity of the composite increase upon irradiation. These changes are attributed to the difference in density of the unirradiated and irradiated zones.
arising out of the restoration of the crystal structure due to the increasing strain within the irradiated polymer.

The unirradiated BaCl₂ doped PVA shows a prominent major peak and smaller peaks. At 100kGy, the major peak slightly shifts to a lower angle which shows the lattice expansion attributed to the introduction of defects in the crystalline phase during irradiation. In addition, at the lower angle side of the spectrum, a new sharp peak appears which was not present in the spectrum for the unirradiated sample. This is attributed to the newly formed fine polymer crystallites in the amorphous zone of the PVA matrix. This result also confirms that the irradiation has a strong influence on the structure of the crystalline regions. The increase in intensity of the peaks with increase in electron dose can also be attributed to scissioning of the polymer chains by which the polymer undergoes some spatial rearrangement. The small fragments may rearrange themselves to form new crystalline zone. On further increase of dose intensity of the many peaks increase in addition to appearance of many small peaks, indicating the increase of crystallinity of the doped PVA due to irradiation. This increase of crystallinity may be attributed to the phenomena of chain scission of the doped PVA sample due to electron irradiation. On further increase of dose, it is observed that most of the newly formed peaks disappear. This result signifies a decrease in the crystalline fraction of the polymer which is attributed to the crosslinking of polymer chains due to high irradiation doses.

The XRD of unirradiated FeCl₃ doped PVA shows a prominent major peak and smaller peaks. After irradiation this major peak slightly decreases its intensity indicates that the amorphous nature of the composite. These results suggest that in the FeCl₃ doped PVA complex containing a cross linking network, the irradiation is not going to affect the microstructure of this already formed cross linked structure.

The XRD of PVA/PVP blend shows a broad amorphous pattern centered at 2θ=20.2°, d=4.3982Å. When it is doped with FeCl₃, the amorphous nature of
the film increases. This behaviour may be attributed to the change of the mode of chelation of the FeCl₃ dopant within the blend. At higher doping level, the spectrum peak is broadened with a significant decrease in its intensity, which indicates that the distribution of the FeCl₃ in the polymer blend matrix became random.

**Thermal Studies:**

The DSC study on pure PVA two endothermic peaks corresponding to $T_g$ and $T_m$. Compared to DSC thermograms of PVA and KCl doped PVA, the irradiated BaCl₂ doped PVA shows multiple endothermic peaks. In case of Pure PVA the observed chain scission at lower doses and crosslinking at higher doses of electron irradiated KCl and BaCl₂ doped PVA affects the $T_g$ of the composite film.

In PVA, during electron irradiation, $T_m$ initially increases and then slightly decreases. This confirms the molecular disorderness within PVA as a consequence of chain scission during irradiation. For the irradiated KCl doped PVA film $T_g$ decreases with a gradual broadening of the melting peak indicating a broad distribution in the crystal sizes and reduction in the crystal ordering caused by irradiation. The gradual decrease in $T_g$ is generally due to the increase in molecular mobility as a result of scissioning of the molecular chains. As the irradiation dose was increased, $T_g$ gradually increases, which suggest the onset of the formation of new radicals and are the precursors of cross linking of the polymer chains.

In the irradiated BaCl₂ doped PVA, a regular decrease in $T_g$ was observed as the electron dose was increased, till a dose of 200kGy, indicating a possible damage of the sample due to irradiation. This decrease in $T_g$ is generally due to scissioning of the molecular chains of the polymer due to electron irradiation. As the electron irradiation dose was increased further, $T_g$ increases slightly. Further increase in $T_g$ was observed when the dose is increased indicating cross linking of the polymer chains.

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Positron Annihilation Studies:

Positron lifetime measurements were carried out on electron irradiated KCl doped PVA and BaCl₂ doped PVA to understand the effect of electron irradiation on the free volume related microstructure.

In the case of electron irradiated KCl doped PVA, except for 100kGy, the o-Ps lifetime $\tau_3$ increases till a dose of 300kGy and thereafter it decreases for higher doses. This suggests the enhancement of free volume size which is attributed to chain scission process within the doped PVA due to irradiation. On further increase of irradiation dose upto 600kGy the onset of cross-linking process of the PVA matrix seems to be dominates over chain scission as a result the free volume size decreases. On the other hand, in irradiated BaCl₂ doped PVA, it is noticed that both $\tau_3$ and free volume size initial increases monotonically up to 200kGy and afterwards decreases at higher doses. The intensity $I_3$ increases continuously in the whole range of electron dose. This variation suggests that the o-Ps lifetime is sensitive to local molecular environment and in particular to the size of the free volume region in which it is localized.

The studies on positron behaviour in the FeCl₃ doped PVA/PVP blend study shows that the doping increases the amorphous nature of the film and both inhibition and quenching of Ps formation occurs within the blend. Because the Fe$^{3+}$ ions are known to promote oxidation of Ps, the intensity ($I_3$), of Ps pick-off annihilation is decreased to a great extent. The linear behaviour o-Ps trapping rate ($1/\tau_3$) with FeCl₃ doping indicates that the quenching process also takes place in this complex system and quenching rate constant has been estimated. Here the positron annihilation results are not reflecting the free volume related microstructure of the film.

Conclusions:

Generally many methods (like doping, blending and irradiation etc) have been applied to tune or modify the physico-chemical properties of a polymer. It is known that the physical and chemical properties needed for a specific
Application can be tuned by adding or doping with a dopant. Here the interaction of the dopant with polymer matrix plays an important role between functional groups of the polymer and the dopant. The modifications in properties due to doping depend on the chemical nature of the doping substances and the ways in which they interact with the host matrix. In recent days electron beam (EB) irradiation is also considered as one of the convenient methods used to tune the physical and chemical properties of a polymer. Here also type of modification depends on the type of radiation and nature of the polymeric system. Another way of modifying the polymer property is by blending. Hence the understanding and processing of polymer with different dopants, irradiation and blending is a field of continuing research. For the present study, a water soluble and easily available polymer PVA has been chosen as the host. Three metal chlorides KCl, BaCl₂ and FeCl₃ with different cationic valency, ionic radius (K⁺ = 1.33 Å, Ba²⁺ = 1.35 Å and Fe³⁺ = 0.64 Å) electro negativity (K⁺ = 0.82, Ba²⁺ = 0.89 and Fe³⁺ = 1.83) are used as dopants. The pure polymer and doped polymers are irradiated with 8MeV electron beam using an electron accelerator, the Microtron. In addition, metal chloride FeCl₃ and an organic NLO compound have been used as the dopant for PVA/PVP blend. The radiation induced microstructural changes in the pure and doped polymer and microstructural changes in the doped blend have been studied with different experimental methods.

The investigations on the radiation induced microstructural studies in pure PVA and doped PVA polymers indicate that the doping and electron irradiation have major role in the modifications of the polymer microstructure and related properties. The doping of the blend PVA/PVP also has a significant role in changing its microstructural properties for specific applications.

FTIR studies on electron irradiated PVA shows that the electron beam accelerates the reaction in the O-H group of PVA leading to cleavage of both C-H and O-H bonds leading to chain scission (degradation). In the case of KCl and BaCl₂ doped PVA, main chain scission is dominant at smaller doses and
crosslinking occurs at higher doses. Degradation process was accompanied by appearance of new UV and FTIR absorption peaks. A gradual color change of these films from white to pale yellow is also confirmed by UV-Vis studies and other optical parameters. XRD studies indicate increase of crystallinity upon irradiation and such changes are attributed to the difference in density of the unirradiated and irradiated zones arising out of the restoration of the crystal structure due to the increasing strain within the irradiated polymer. Thermal studies show that the thermal behaviour is different for different irradiated doped polymers. The variation of melting behaviour and glass transition temperature reflects these changes.

Positron lifetime measurements carried out on electron irradiated KCl and BaCl₂ doped PVA suggests that the enhancement of free volume size which is attributed to chain scission process within the irradiated composite. On further increase of irradiation dose the onset of cross-linking process of the PVA matrix seems to be dominates over chain scission and affect the free volume properties. Positronium (Ps) in polymers is known to be influenced by many factors, such as temperature, positron irradiation, doping, chemical nature, electric field and irradiation. The studies on positron behaviour in the FeCl₃ doped PVA/PVP blend shows that the doping increases the amorphous nature of the film and both inhibition and quenching of Ps formation occurs within the blend.

From this study it is concluded that the microstructure as well as polymeric properties can be modified using electron irradiation. These microstructural modifications depend on the chemical nature of the polymer, the dose applied etc.

**Scope for Future Work:**

As the advanced technologies expand, the materials with enhanced properties are to be designed to perform more complex and efficient tasks. In this regard, ionizing radiation has been found to be a widely applicable in
modifying the structure and properties of polymers, and can be used to tailor
the performance of either bulk materials or surfaces. The research in polymer
radiation chemistry has led to numerous applications of commercial and
economical importance, and the work remains active in the application of
radiation to practical uses involving polymeric materials. In view of this, the
above studies show that the irradiation of polymeric materials modifies its
properties which can be used for specific applications. Among the ionizing
radiations, high energy electron beam irradiation is one of the efficient tool to
induce changes in optical properties (such as absorbance, optical band gap),
chemical structure, crystallinity, solubility, variation in crystallite size, chain
scission and crosslinking. It is observed that all these microstructural changes
affect the macroscopic properties of the modified polymers.

Irradiation of polymers with other types of ionizing radiations like heavy
ions, gamma rays, protons, laser beam and UV irradiation has inspired much
interest in scientists and engineers due to induced improvement in optical,
electrical and mechanical properties. In view of this there is a lot of scope for
the study of modification of above studied polymeric materials using such
types of radiation. Hence the author wishes to continue the work to understand
the radiation induced microstructural studies of doped polymeric materials with
different radiations.

Polymer blends have recently become one new area of macromolecular
application and research. There has been increasing interest in blending with
different homopolymers to obtain new products having some of the
characteristic properties of each of their component. The studies on the
transition metal chloride and chalcone doped PVA/PVP blend suggest that the
microstructural properties of the blends can be modified by different dopants.
In addition, to know the radiation induced microstructural changes in the
blends and doped blends, the author wishes to continue the work to investigate
the modifications due to irradiation of blends and doped blends with different
ionizing radiations.
Recently, one of the most advances in polymer science is in the field of nanocomposites. A remarkable growth of interest on nanocomposite materials has been observed owing to its many potential applications. Nanocomposites often exhibit physical and chemical properties that are dramatically different from conventional micro-composites. Today, the polymer nanocomposites have emerged as a promising group of such materials. The polymer systems containing various nanoparticles reveal unique optical, thermal, electrical and mechanical properties as a result of nano-filler-matrix interactions. These ultralight materials with specific properties could find applications in many fields of industry. Along with this, the concept of hybrid organic-inorganic nanocomposites exploded the expansion of soft inorganic chemistry processes. Indeed, the mild synthetic conditions offered by the casting method allow the mixing of inorganic and organic components at the nanometer scale. Recently optical studies performed on polymer nanocomposites have evolved towards different objectives such as development of materials with specific optical properties based on the properties of organic or inorganic chromophores. In view of this there is a lot of scope for the study of polymer nanocomposites. Hence the author wishes to continue the work mentioned above to understand the nanocomposite materials with different environment like different radiations such as energetic electrons, heavy ions, gamma rays, UV-radiation etc.

Thus the polymeric materials have a proven potential in all fields of life and the modification of their properties is an important aspect from the point of view of different applications. In view of this, the author wishes to study the radiation induced microstructural studies on pure and doped polymers, pure and doped blends and nanocomposites.