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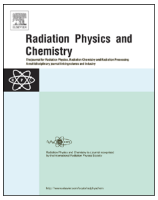

A comparative study of the effect of Ni^{9+} and Au^{8+} ion beams on the properties of poly(methacrylic acid) grafted gum ghatti films

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HIGHLIGHTS

- The effect of 120 MeV Ni^{9+} and Au^{8+} ion beams irradiation on grafted hydrogel was studied.
- XRD pattern shows a decrease in intensity of peak position with increase in ions fluence.
- FTIR spectrum shows an overall reduction in intensity of typical bands.
- The decrease in IDT and FDT shows thermal changes in the grafted hydrogel.

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ABSTRACT

A systematic comparative study was carried out for the induced changes in the chemical, structural, morphological and thermal properties of poly(methacrylic acid) grafted gum ghatti i.e. [Gg-cl-poly (MAA)] material by irradiation of 120 MeV Ni^{9+} and Au^{8+} ions at various fluences ranging from 3×10^{11} to 3×10^{12} ions/cm^2. The degradation of the material was observed after ion irradiation. A significant loss of crystallinity and change in the crystallite size was observed in irradiated samples of Gg-cl-poly(MAA). The changes in chemical properties and surface morphology were observed by Fourier transform infrared spectroscopy and scanning electron microscopy respectively. The magnitude of the effect of the irradiation was observed to be greater in the case of Au^{8+} ions irradiation than those of Ni^{9+} ions irradiation due to the high electronic energy loss of the Au^{8+} ions in the grafted samples.

1. Introduction

In early years, irradiation induced material modifications were made using low ionizing beams comprising mainly of fast electrons, low energy ions, gamma rays and X-rays. Interest on modification of materials has increased very significantly with the availability of heavy ion accelerator of higher energy all over the world (Jain and Agarwal, 2011). When swift heavy ions (SHIs) penetrate in a target material, it slows down mainly via two independent processes (Krasheninnikov and Nordlund, 2010): (i) direct transfer of ion energy to target atoms through elastic collisions, i.e. nuclear energy loss (S_n), and (ii) electronic excitation and ionization of target atoms or inelastic collisions, i.e., electronic energy loss (S_e). Both the processes occur simultaneously and their contribution to the total energy losses of the traverses ion is given by stopping power i.e. $(-dE/dx)_e$, which is a function of energy, linear energy transfer, ion fluence, mass, charge and the nature of the target material (Calcagno et al., 1992). The former is the dominant mechanism at low energies regime ($\sim$keV/nucleon) whereas the inelastic collisions dominate at high energies (>1 MeV/nucleon) where the transfer of atoms due to elastic collisions are irrelevant. The Coulomb-explosion model (Wang et al., 1994) and the thermal-spike model (Toulemonde et al., 1992) are generally used to understand the mechanisms of the material modifications induced by heavy ions interaction with the target material. Intense electronic energy deposition is responsible for the modification in material properties. It can produce columnar defect, point defect and even amorphous tracks along the path of its motion (Krasheninnikov and Nordlund, 2010). Apparently, swift

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heavy ion (SHI) can be used to bring about new properties not accessible with conventional chemical, radiochemical or physical means (Porte-Durrieu et al., 2000; Chawla et al., 2006). Generally, target ionisation causes bond breakage; the formed free radicals are expected to come at rest and may react in a molecular site of a different type from their original site (Picq et al., 1998). It is well reported that these free radicals are accountable for the most of the chemical transformations observed in the polymeric materials such as chain scission, cross-linking and double or triple bond formation. The extent of the modifications induced by penetrating of the heavy ions through the solid depends on the energy deposited by the particle, i.e., on the charge, mass and energy of the incident particle as well as on the polymer properties (crystallinity, chemical composition, molecular weight, density, etc.) (Rouxhet and Legras, 2000). In polymers, gaseous species also evolve from the ion track because of chain scission and crosslinking (Singh et al., 1999, 2007; Bedell et al., 1990; Hnatowicz et al., 1994). The rise of these complex phenomena deeply affects the polymer macromolecular structure and morphological properties with no significant changes in its composition (Lounis-Mokrani et al., 2003). In past few years, the effect ion implantation in polymers has also been investigated (Popok et al., 1997; Dhillon et al., 2013). It has been found that ions implantation may reduce the crystallinity, induces cross-linking and produces carbonyl groups on the polymers, which results in polymer degradation (Loh et al., 1988; Biswas et al., 1999). Various studies in the field have shown prominent surface carbonization and splitting of chemical bonds on the side of the polymer chain in ion implanted polymer films (Kaplan et al., 1984; Bedell et al., 1990). Popok (2012) has discussed various important aspects of ion stopping, latent track formation and change of structure as well as composition of organic materials after ion implantation in his review article.

There are very few reports available in the literature, which characterize the chemical, structural, thermal and morphological evolution in SHI irradiated hydrogels (Huq et al., 2012; Tiwari et al., 2013; Kaith et al., 2014). However, plethoras of reports have been found in literature on the use of light and heavy ions for the modifications of different polymeric materials. Dargaville et al. (2003) reviewed high energy radiation induced grafting of fluoropolymers and the analytical methods available to characterize the graft copolymers. Various authors reported that saccharide monomers decompose under exposure to low-energy electrons (Ryzhkova et al., 2011). The effects of irradiation on controlled drug delivery and controlled drug release systems have been reviewed by Razem and Katusin-Razem, 2008. Tanaka et al. (2011) concluded that ion-beam irradiation is a useful technique for improving the surface properties of biodegradable polymers without missing the bulk properties. In our previous group work, we have carried out the detailed investigation of the effects of irradiation on the properties of different polymeric materials (Kumar et al., 2012a, 2012b, 2012c; Ali et al., 2013; Sonkawade et al., 2010).

In the present study cross-linked hydrogel [Gg-cl-poly(MAA)] were synthesized. Elsewhere communicated optimized process parameters (viz. initiator, cross linker and monomer concentration, reaction time, solvent concentration, pH and vacuum) have been employed during synthesis to ensure an optimum percentage swelling. The synthesized samples of Gg-cl-poly(MAA) were irradiated with Ni^{9+} and Au^{8+} ion beams and investigated for modifications in structural, chemical, surface and thermal properties. The fluences were used in the range 3×10^{11}–3×10^{12} ions/cm^2. The role of linear energy transfer (LET) of both the ion species is also reported. The irradiated hydrogel samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravemetric analysis (TGA). An attempt has been made to correlate the results with reported data.

2. Experimental

2.1. Materials

Gum ghatti (Gg) [backbone] was purchased from Sigma Aldrich. Ammonium persulfate (APS) [initiator], *N,N′*-methylene-bis-acrylamide (MBA) [crosslinker], methacrylic acid (MAA) [monomer] and acetone were purchased from Merck India. All the chemicals were used as received without further purification. The deionized water was used for all the reactions.

2.2. Sample preparation

A polymer matrix composed of Gg-cl-poly(MAA) was prepared by using MBA as a crosslinker and APS as an initiator under vacuum oven. In a typical experiment, 0.5 g gum ghatti was dissolved in 10 ml of double distilled water in a reaction flask. To this reaction mixture, a calculated amount of APS and MBA was added followed by drop-wise addition of MAA under continuous stirring. The reaction container was kept in a vacuum oven at 60 °C for 2.5 h and the resulting product was freed from homopolymer through solvent extraction using acetone. Finally, the product was dried in a hot air oven at 50 °C. The monomer concentration, initiator concentration, cross linker concentration, polymerization time, solvent, pH of the reaction mixture, temperature and vacuum were kept constant at 2.36×10^{-4} mol/l, 0.0131 mol/l, 0.0324 mol/l, 150 min, 12 ml, 7, 60 °C and 450 mm-Hg respectively (optimized values). The grafted copolymer exhibited percentage grafting and swelling of 55% and 1613% respectively. The functionalized polymer unit in the hydrogel can be determined by percentage grafting and FTIR spectroscopy. The mechanism of the PMAA onto gum ghatti is given in Scheme 1. The thickness of the cross linked hydrogel films was 50 ± 5 μm.

2.3. Swift heavy ions irradiation

The Gg-cl-poly(MAA) films with optimized process parameters (mentioned above) were exposed to 120 MeV Ni^{9+} and Au^{8+} ions beam from the 15 UD Pelletron accelerator at Inter University Accelerator Centre, New Delhi, India. The irradiations were carried out at room temperature under high vacuum conditions ($\sim 5 \times 10^{-6}$ Torr). The ions fluences were varied from 3×10^{11} to 1×10^{13} ions cm^{-2}. The irradiation time has been calculated by using the formula $t = \phi Aqe/I$ (where ϕ is the fluence, A is area of irradiation and I is the current in particle nanoampere (pnA)). The fluence ϕ in the present work can be calculated by the formula $\phi =$ ions s^{-1}/area. Ion fluence calibration was achieved by determining the beam current with a Faraday cup. The uncertainty in the ion fluence measurement can be up to 20% due to the ambiguity in the ion beam area, fluctuation in the current, integrated charge etc. Irradiations were performed at a low ion current of 0.5 pnA to avoid the thermal degradation of the samples.

2.4. Instrumental analysis

The XRD analyses were performed at room temperature by using a Bruker AXS, X-ray diffractometer. The X-ray beam was nickel filtered Cu-K_α ($\lambda = 1.542$ Å) radiation operated at 30 kV and 30 mA. Data were obtained from 2θ of 10° to 50° at a rate of 1°/min with a step size of 0.02°. FTIR analysis was undertaken in order to study the damage of Gg-cl-poly(MAA) under SHI irradiation and was performed in the transmission mode. FTIR spectra of samples were recorded in KBr pellets on Nexus 670 FT-IR system. SEM images were obtained using a JEOL JSM-6490LV microscope at 25 kV after covered with a thin layer ($\sim$20 nm) of sputtered gold.