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In-situ investigation of polyvinyl formal irradiated with GeV Au ions

T. Seidl [a,b,*], O. Baake [a], U.H. Hossain [a,b], M. Bender [b], D. Severin [a,b], C. Trautmann [b], W. Ensinger [a]

[a] Technische Universität Darmstadt, Department of Materials and Earth Sciences, Materials Analysis, Petersenstr. 23, 64287 Darmstadt, Germany
[b] GSI Helmholtz Centre for Heavy Ion Research, Materials Research, Planckstr. 1, 64291 Darmstadt, Germany

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ABSTRACT

Polyvinyl formal (Formvar®) foils were irradiated with 5.4 MeV/u Au ions and analysed in-situ by residual gas analysis and infrared spectroscopy. The experiment was performed at the new materials-research beamline (M-branch) at the universal linear accelerator of the GSI Helmholtz Centre in Darmstadt (Germany). Simultaneously analysing outgassing fragments and changes within the irradiated polymer film allows monitoring details of the degradation process.

Ion-induced degradation of polyvinyl formal is characterized by fragmentation of side chains of the polymer backbone. The infrared spectra show the formation of unsaturated hydrocarbons and ketones. A possible degradation mechanism is proposed including the production of enols as reported earlier for degradation of polyvinyl alcohol exposed to gamma radiation.

1. Introduction

When exposed to high-energy particle beams, many insulators respond by dramatic degradation. Radiation effects in the MeV to GeV energy region are dominated by electronic excitation processes, because the ion projectiles lose their energy mainly by interaction with the electronic subsystem of the target. The linear energy transfer of heavy ions is of the order of few keV/nm which is sufficiently large to break all atomic bonds within a nanometric cylindrical zone along the ion trajectory. This work concentrates on polymers which are known to strongly degrade under the bombardment of swift heavy ions. The ion radiation induces the formation of radicals and ionized species which react in a complex mechanism with the organic polymer system [1,2] resulting in chain scission, cross linking, creation of unsaturated hydro carbons, carbonization as well as the loss of volatile degradation products [3,4]. As a consequence, the physical and chemical properties of the polymer are changed including e.g. the insulation behaviour and mechanical strength [5]. In contrast to these detrimental modifications, the ion-track nanotechnology takes advantage of the modified material in the ion track by transforming the cylindrical damage zone of each ion track into an open nanochannel by means of selective chemical etching [6–9].

Radiation damage and degradation of functional properties play a crucial role for materials used in high dose environment such as satellite or spacecraft components in space as well as in future high power and high energy particle accelerators [10]. To simulate the effect of cosmic rays or high energy projectiles, irradiation experiments can be performed at existing ion beam facilities as for instance the Universal Linear Accelerator (UNILAC) at the GSI Helmholtz Centre for Heavy Ion Research (Darmstadt, Germany). The facility provides ion species from hydrogen up to uranium in the energy range from 1.4 to 11.4 MeV/u. Most recently, three new beamlines have been installed at the so-called M-branch housing numerous in-situ analytical methods for irradiation experiments dedicated to materials research. Beamline M1 provides high-resolution scanning electron microscopy (HRSEM) for in-situ sample inspection [11]. Monitoring beam-induced structural changes is possible at beamline M2 by means of in-situ X-ray diffraction (XRD). The irradiation experiments presented in this work were performed at beamline M3 where in-situ infrared spectroscopy can be combined with residual gas analysis. Both techniques are most suitable to follow ion-induced degradation processes in polymers [12,13]. Such in-situ investigations profit from the fact that (1) they provide quantitative results at a fixed sample position (important in case of inhomogeneous film thickness) and (2) for analysis the samples remain in vacuum, thus post-degradation effects due to oxygen can be avoided. Furthermore, by recording degradation effects of a given sample with increasing ion fluence allows time and cost efficient experiments.

This article focuses on the new installation at the M3-beamline and reports first results on polyvinyl formal (Formvar®) insulation material. This polymer plays an important role as cable insulation of the future SIS100/300 superconducting magnets for the

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* Corresponding author at: Technische Universität Darmstadt, Department of Materials and Earth Sciences, Materials Analysis, Petersenstr. 23, 64287 Darmstadt, Germany. Tel.: +49 6159 712175; fax: +49 6151 166378.
E-mail address: t.seidl@gsi.de (T. Seidl).

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FAIR-project [14]. During long-term operation of the FAIR facility some accelerator components will be exposed to a high radiation level. Understanding radiation induced degradation processes is the key for better lifetime estimations of sensitive components.

2. Experimental

2.1. Material

As sample we used a 20-μm thick foil of polyvinyl formal prepared by dissolving 4 g of polyvinyl formal powder (Formvar® from Agar Scientific, Ltd.) in 50 ml of solvent dichloromethane (CH_2Cl_2). The monomer unit of polyvinyl formal is shown in Fig. 1. The solution was continuously stirred for about 24 h at room temperature to ensure homogeneous mixing of the solvent. The film was grown on a pre-cleaned glass substrate by dripping the polymer solution onto the glass surface and streaking the drop with a squeegee to an area of about 10 cm^2. After solvent evaporation in air for 24 h, the polymer sample was cut into small pieces and carefully removed from the glass substrate. The resulting transparent film is continuous and has a homogeneous thickness of 20 ± 2 μm.

2.2. Irradiation

The irradiation experiment was performed at the M3 beamline of the UNILAC housing different beam monitoring systems. The base pressure without beam is typically of the order of 10^{-7} mbar. Before reaching the sample, the slightly defocused beam passes through an aperture consisting of a pair of variable *x*–*y*-slits controlled by individual stepping motors. Each slit position can be adjusted within a precision of 0.1 mm. The size and homogeneity of the beam is visualized using a luminescence screen (distance between screen and sample ~150 cm). During irradiation, the ion flux is monitored by a secondary electron transmission monitor SEETRAM (consisting of three 1-μm thick Ti foils) which is calibrated with a Faraday cup (resulting flux uncertainty ~20%).

The sample irradiation and simultaneous analysis is performed in the multipurpose diagnostic chamber housing an infra-red spectrometer and a residual gas analyser (Fig. 2). The polymer samples (maximum four foils of size 1 cm^2) are mounted on a nearly free-standing sample holder which is attached to a cooling finger in the centre of the chamber. The closed-cycle refrigerator allows experiments down to 10 K (minimum temperature without beam). The sample holder arrangement can be moved upwards by 110 mm and rotated around ±180°. The irradiation was carried out with 5.4 MeV/u Au ions using a beam structure of 5 Hz and 3 ms pulse length. The mean flux was about 8×10^8 ions/cm^{2}s, the accumulated fluence 1×10^{12} ions/cm^2. The range of the Au ions in polyvinyl formal (density ~1.3 g/cm^2) is about 80 μm, thus by far larger than the thickness of the foil.

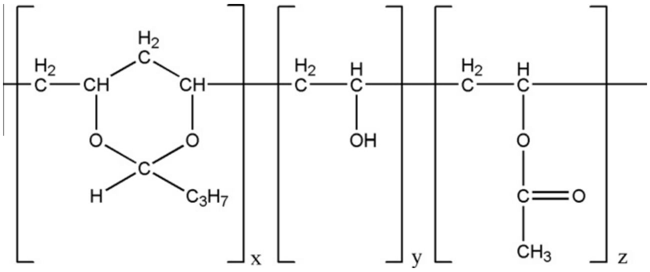

Fig. 1. Structure of polyvinyl formal (Formvar®) monomer unit.

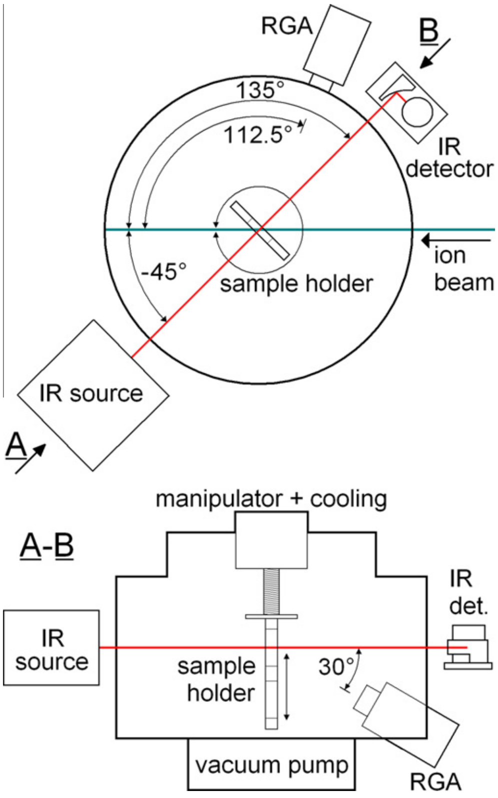

Fig. 2. Schematic side and top view of the multipurpose analysis chamber at beamline M3 housing the sample stage, infra-red (IR) spectrometer, and residual gas analyser (RGA).

2.3. Analysis

The infrared (IR) light provided by the Fourier transform infrared (FTIR) spectrometer (NICOLET 6700) passes through the irradiation chamber under an angle of 45° with respect to the ion beam. The entrance and exit windows consist of 4-mm thick ZnSe crystals. The IR source and the detection unit are both installed outside of the irradiation chamber (Fig. 2). IR spectra were recorded in the wave number range from 4000 to 400 cm^{-1} coadding 4 scans with a spectral resolution of 2 cm^{-1}.

For residual gas analysis (RGA) a quadrupole mass spectrometer (E-Vision Plus, EVP-220-000) was used providing a detection range from 6.7×10^{-14} to 6.5×10^{-4} mbar for mass-to-charge (m/z) values between 1 and 200. Ionization of the residual gas components is achieved with an RGA accelerating voltage of 70 eV. The analyser is mounted at 112.5° with respect to the ion beam and is tilted 30° in azimuthal direction (Fig. 2). The analyser-to-sample distance is about 10 mm.

IR and RGA background spectra were measured before starting the irradiation, the analysis of the residual gas was continuously monitored with and without beam. In the initial phase of irradiation, full mass spectra were taken. For subsequent long term monitoring, the 15 most prominent and relevant masses were selected. IR spectra were recorded in intervals during short beam stops.

3. Results and discussion

3.1. Residual gas analysis

The RGA spectra before and during ion irradiation of polyvinyl formal are shown in Fig. 3. The spectrum before the start of the irradiation is dominated by H_2O and CO molecules, but also con-