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Mass spectrometric comparison of swift heavy ion-induced and anaerobic thermal degradation of polymers

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ABSTRACT

The study of polymers irradiated by highly energetic ions and the resulting radiation-induced degradation is of major importance for space and particle accelerator applications. The mechanism of ion-induced molecular fragmentation of polyethylene, polyethyleneimine and polyamide was investigated by means of mass spectrometry and infrared spectroscopy. The results show that the introduction of nitrogen and oxygen into the polymer influences the stability rendering aliphatic polymers with heteroatoms less stable. A comparison to thermal decomposition data from literature reveals that ion-induced degradation is different in its bond fracture mechanism. While thermal degradation starts at the weakest bond, which is usually the carbon-heteroatom bond, energetic ion irradiation leads in the first step to scission of all types of bonds creating smaller molecular fragments. This is due to the localized extreme energy input under non-equilibrium conditions when the ions transfer kinetic energy onto electrons. These findings are of relevance for the choice of polymers for long-term application in both space and accelerator facilities.

1. Introduction

Insulators used in space in satellites, telescopes and vehicles are exposed to all kinds of radiation, including highly energetic particles of Galactic Cosmic Rays (Gaisser, 1990). Accelerator facilities and nuclear power plants demand the same requirements on insulators, considering their high radiation environments. The new *Facility for Antiproton and Ion Research* (FAIR) which is presently under construction at the *GSI Helmholtzzentrum für Schwerionenforschung* in Darmstadt, Germany, is designed to deliver beams of radioactive and stable heavy particles up to uranium ions with intensities as high as 10^{12} ions s^{-1} and energies up to 20 GeV per nucleon (Gutbrod et al., 2006). During beam operation, devices such as the superconducting magnets will be exposed to high-dose radiation of X-rays, gammas, neutrons, and to some extent to charged particles, including ions of low to medium mass. Radiation-induced degradation in organic materials depends primarily on the absorbed dose, but also on the type of radiation. The type can differ in penetration depth, intensity, and spatial energy deposition as well as environmental factors such as temperature and atmosphere (Severin et al., 2010). The radiation field around accelerators is predominantly composed of light particles, such as neutrons and protons. However, even heavier elements, such as carbon, can be found. The latter are generated from primary particles which fragment when they hit the beam line tubes. This leads to a significant interest in the influence of particle radiation on insulation materials. Ceramics and polymers are the most common materials used as insulators for superconducting magnets. Ceramics that are known to have the advantage of a higher radiation hardness compared to polymers might seem to be the better choice. However, beam conducting magnet superconductors operate at room and low temperatures, which increases the importance of the difference of thermal expansion coefficients in construction materials significantly (Bauer et al., 1998). Due to a very low ductility and a brittle structure of ceramic materials, the slightest variance in thermal expansion coefficients compared to the conducting material might cause ruptures/structural damage in the superconducting magnet insulation. Though polymers can be used in the harshest environments for insulation purposes and do not suffer from problems with expansion upon cooling, they are rather prone to highly energetic radiation. Therefore, it is of interest to study their stability against particle radiation.

The general effects of irradiation with ion beams of MeV-GeV kinetic energy on polymers are well documented in literature, e.g. (Hossain et al., 2014a, 2014b; Balanzat et al., 1994). Modification of aliphatic polymers through swift heavy ions has been investigated by several groups, e.g. by (Balanzat et al., 1994, 1996) on polyethylene (PE) and polystyrene (PS), or on polymethyl methacrylate (PMMA)

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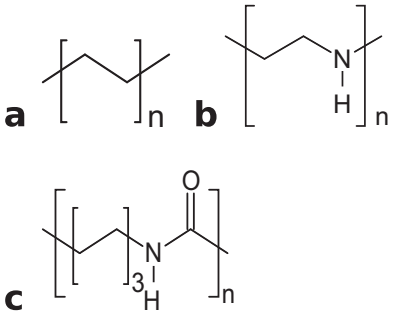

Fig. 1. Scheme of the chemical structures of a) PE, b) PEI and c) PA6.

(Hossain et al., 2014a) and different polyvinyls (PVA, PVAc, PVF) (Hossain et al., 2014b). The interaction of energetic ion beams with polyimide (Kapton™) has been studied by several groups, investigating radiation-induced degradation and damage track formation by means of spectroscopy (e.g. IR, UV–Vis, Raman), high-resolution microscopy (e.g. scanning force and transmission electron microscopy) and other techniques (Severin et al., 2010, 2005). However, there is still a lack of knowledge regarding the radiation hardness of particular polymers under irradiation with heavy ions, especially in terms of their molecular degradation mechanism.

In general, each ion produces a track of structurally changed bulk material along its trajectory, whose core is typically a few nm in diameter and surrounded by a cylindrical halo-like degraded area. This zone shows known changes of morphological characteristics (Adla et al., 2001). This enables a modification of any polymer film beyond the surface into the bulk material (Fleischer et al., 1975). It can even induce the creation of alkynes, which was revealed through studies by means of infrared (IR) spectroscopy and is not observed in classical radiation experiments (Steckenreiter et al., 1999).

In this study, we concentrate on radiation-induced degradation effects of three types of polymers. Polyethylene (PE), polyethyleneimine (PEI), and polyamide (PA6) were exposed to highly energetic heavy ions, simulating harshest radiation environment and providing estimates of the performance under the worst case scenario. PE is the simplest polymer, homogeneously structured and consisting only of carbon and hydrogen (see Fig. 1a). It is commonly used in many applications, either as high density Polyethylene (HDPE), linear low density polyethylene (LLDPE) or low density polyethylene (LDPE). Typical applications are electrical insulation and packaging. The structure of PEI is similar to PE, containing nitrogen as an additional heteroatom (Fig. 1b), whereas PA6 introduces the amide group, containing nitrogen and oxygen as additional heteroatoms (Fig. 1c). PEI is used in detergents, adhesives, water treatment agents and cosmetics. PA6 was chosen to evaluate the difference, when a more complex functional group is introduced to the carbon-hydrogen-backbone. PA is used as fibres, in car components and food packaging.

It is necessary to compare the degradation behavior of the polymers and understand the role of the different elements and bond types. The degradation was compared to anaerobic thermal decomposition of the polymers, to evaluate the effect of irradiation under non-equilibrium conditions.

Those three polymers were chosen due to their increasing complexity building up on each other. Whereas PE is a simple hydrocarbon polymer, PEI already has nitrogen as a heteroatom in the repetition sequence. In the case of PA the amide group with an oxygen as a further element is introduced. Hence, it is helpful to analyze the similarities and differences during irradiation experiments to enable the design of insulating polymers with increased radiation hardness. In addition, the experimental data on radiation-induced decay presented here are of special concern for the superconducting magnets of the ion synchrotron SIS100 of the FAIR facilities.

2. Experimental

2.1. Materials and irradiation

Commercial-type foils of PE and PA6 were purchased from Goodfellow, providing a thickness of 20 µm. The polymer foils were, prior to irradiation experiments, cut to squares, with a side length of 2.5 cm. These samples were irradiated under high vacuum with $^{197}Au^{25+}$ ions with an energy of 11.1 MeV/u, corresponding to a total kinetic energy of ca. 2.2 GeV, at the universal linear accelerator (UNILAC) of GSI *Helmholtzzentrum für Schwerionenforschung*. The experimental setup with sample chamber and in situ spectroscopy has been described elsewhere (Baake et al., 2011). The PEI foils were produced with a saturated solution of PEI (Polysciences) in

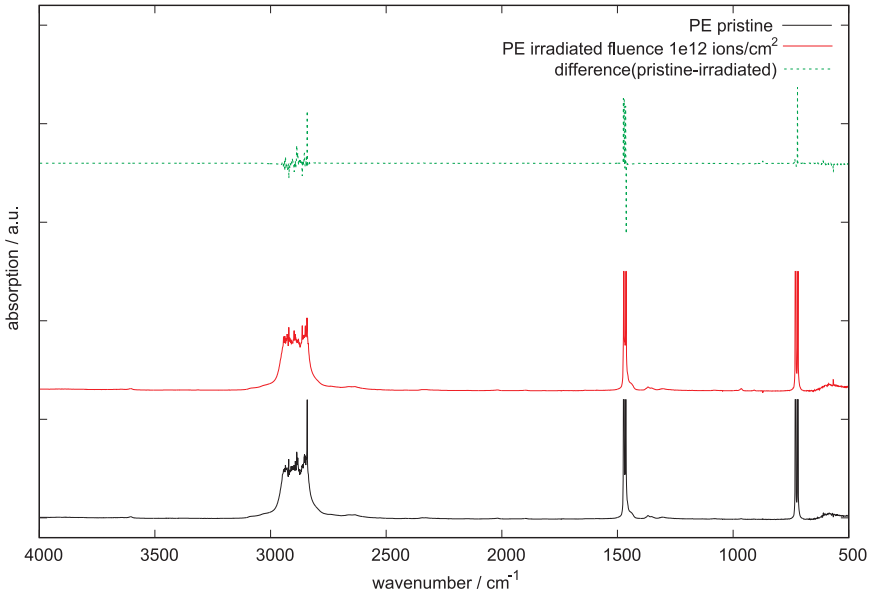

Fig. 2. An IR spectra overview of an unirradiated sample of PE (bottom), an irradiated sample with $1x10^{12}$ ions/cm^2 (middle) and the calculated difference (top) between the two spectra. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)