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Microstructure evolution of polyimide films induced by electron beam irradiation-load coupling treatment

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ABSTRACT

Polyimide films are widely used in space with extreme environments, where high energy beam irradiation and corresponding coupling treatment could occur. The combined effect of high energy electrons (1.2 MeV) and high tensile stress (50 MPa) on the degradation behavior of polyimide films was studied by means of scanning electron microscopy, atomic force microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and mechanical testing. The degradation of polyimide films was evaluated by analyzing the microstructure and mechanical properties. The results indicated that the external tensile stress and irradiation coupling treatment resulted in the breakage of a larger number of chemical bonds and greater deterioration of the surface quality when compared with the irradiated polyimide samples. After irradiation-load coupling treatment, numerous micro-cracks were formed on the polyimide surface, facilitating the diffusion of oxygen into polyimide films and thus increasing the probability of free radical reactions. Moreover, the coupling treatment led to a more significant decrease in tensile strength and elongation of polyimide films by 10% and 35%, respectively. The mechanism of molecular chains' scission and crosslinking as well as correlations between molecular chains and mechanical performances were discussed. The obtained results indicated that the external tensile stress accelerates the degradation process during electron beam irradiation; thus, the tensile stress potentially seriously deteriorates polyimide film properties in irradiated environments.

1. Introduction

Due to its remarkable thermal stability and mechanical properties, polyimide films have been widely used as structural materials in a number of fields with extreme conditions, such as in space missions and nuclear installations, e.g. in thermal blankets, shielding, and reflective materials [1,2]. The high-energy charged particles in space, such as electrons, protons, and heavy ions, might affect the microstructure of polyimide significantly, and the corresponding changes in the polyimide have to be analyzed [3–6]. When exposed to energized particles, the irradiation effect on the polyimide could be classified into ionization and displacement effect. The charged particles, such as electrons, protons, and heavy ions, might lead to an ionization effect on the polyimide. Meanwhile, the displacement damages in polyimide would be caused by protons and heavy ions. Generally, the ionization and displacement effect induced by energized particles could lead to scission and crosslinking of molecular chains, and thus change the microstructure of the polyimide. These complex chemical reactions may lead to the breakage of original chemical bonds in polyimide and the formation of new chemical bonds as well as volatile species [7,8]. Further, the free radicals induced by irradiation would recombine and react with oxygen in the polyimide [9,10].

Previous studies confirmed that the tensile strength and elongation dropped over 50% after 3 MeV proton irradiation [11]. Further, it also decreased the glass transition temperature due to the scission of molecular chains in the polyimide [12]. It was reported that the energized electrons could decrease the surface roughness and deteriorate the mechanical properties and thermal stability due to the breakage of chemical bonds in the polyimide [13–15]. Further, some researchers performed experiments with electron and proton irradiation in air to study the microstructure evolution and degradation behavior of polyimide films, which also provided useful information for the application of polyimide films in space [12,15,16]. The heavy ions also led to severe polyimide degradation and new chemical bonds were detected after

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irradiation [17]. Consequently, the surface quality, and mechanical, optical, and dielectric properties of the polyimide tended to degrade after irradiation with charged particles and thus influence the durability of the components [3,18–23].

Generally, when analyzing the polyimide degradation behavior, studies have mainly focused on the factors related to irradiation such as particle types, irradiated doses, and accelerating voltage. However, the components in extreme environments based on the polyimide matrix (e.g., solar panels and sail) not only get irradiated by the energized particles but also experience tensile stress, which might lead to creep and plastic deformation in the polyimide matrix. Further, the molecular chains in polyimide films tend to be stretched under tensile stress. In this case, the degradation behavior of irradiation-only polyimide films might be different from that of films treated with the combination of external tensile stress and high-energy irradiation. According to previous reports, the tensile stress level of 1.4 MPa was based on the nominal stress of the base films of the ADEOS-I solar panels [24]. However, in order to estimate and investigate the performance and microstructural evolution in space with extreme environments, most researchers used higher tensile stress levels and high loading conditions. Results have shown that low-energy (200 keV) electron beams and tensile stress (<7 MPa) coupling treatment had little impact on the mechanical properties [24,25]. However, it was suggested that the tensile stress led to increasing roughness in polyimide and initiated rapid degradation, especially when a high load (≥40 MPa) was applied [23,26]. Therefore, the stress state is an important factor to be considered in order to maintain the reliability in complex environments. However, few studies have investigated the irradiation evolution and mechanical performance after combination treatment with high-energy electron beam irradiation and high tensile stress.

It can be concluded from the discussed previous work that the tensile stress could significantly degrade polyimide during irradiation in specific conditions; however, few previous studies have considered the effect of tensile stress during electron beam irradiation. In this study, the effect of coupling treatment is investigated by applying a combination of high-energy electron beam irradiation (1.2 MeV) and high tensile stress (50 MPa). The aim of this work is to shed light on the effect of tensile stress as an external factor on the microstructure and mechanical properties after irradiation-load coupling treatment.

2. Experimental

Polyimide films (50 μm thick) composed of pyromellitic dianhydride (PDMA) and 4,4′-oxydianiline (ODA) structure were supplied by China Academy of Space Technology. The corresponding chemical unit of PMDA-ODA is shown in Fig. 1. The polyimide film was anisotropic, which was manufactured by the tape casting process and then stored in rolls. The samples were cut from the center with dog-bone shapes for the following irradiation and load coupling experiment. The longitudinal direction of the polyimide sample, namely the loading direction in tensile tests, was in accordance with machine direction of the film in order to prevent anisotropy effects. The detailed dimensions of specimens are shown in Fig. 2.

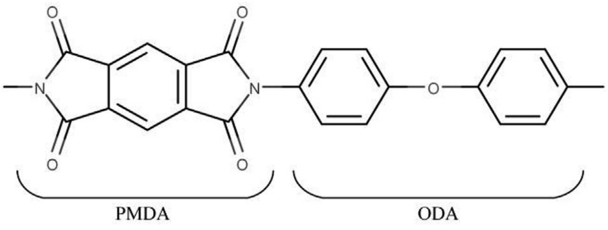

Fig. 1. Schematic of the polymeric repeating unit of PMDA-ODA.

The electron beam irradiation was carried out in a ground-based simulation facility at the Technical Physics Institute of Heilongjiang Academy of Sciences. The irradiations were carried out in air and at room temperature. The effective electron beam area is about 100 mm × 500 mm. The electron fluence in this study varied from 5×10^{14} to $1 \times 10^{16}\,\mathrm{cm}^{-2}$ with an accelerative voltage of 1.2 MeV. According to the ESTAR database from the National Institute for Standards and Technology (NIST), the range of 1.2 MeV electrons in polyimide is 4.2 mm [27]. It can be concluded that most high-energy electrons can penetrate through the 50 μm polyimide film and the entire film can be damaged by electron irradiation.

The schematic of irradiation-load coupling system is shown in Fig. 2. The loading tensile stress was controlled by the weight and sliding system, which was calibrated by using a force sensor before irradiation. According to previous studies, it could be set as an elastic region of the polyimide film below the yield stress [23]. When we set the yield point stress at 3% strain in this study, as illustrated in Dupont's report, the plastic region starts at around 50 MPa for the pristine polyimide film according to the stress-strain curve [28]. In order to increase the tensile load and maintain the treated polyimide samples in the elastic region, the tensile stress was set as 50 MPa.

The irradiated surface morphology was observed by scanning electron microscopy (SEM, SUPRA 55 SAPPHIRE, Zeiss) and atomic force microscopy (AFM, Bruker Dimension Icon). The surface roughness (R_a) was calculated from an arithmetic mean with scanned areas of $3 \times 3\,\mu\mathrm{m}^2$ via AFM.

The phases of irradiated samples were identified by Panalytical Empyrean X-ray diffraction (XRD) with a copper target. The scan step was 0.05° and the counting time was 0.4 s. The molecular structure and chemical bonds transformations after irradiation were evaluated by Fourier transform infrared (FT-IR, Nicolet 5DXC) spectroscopy in the range of 600–2000 cm^{-1} and X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific) with a detection depth of 2 μm and 10 nm, respectively. Before analyzing high-resolution XPS spectra, the binding energy of 284.5 eV for the C1s peak was used for instrumental calibration.

The mechanical properties of the irradiated polyimide films were measured at the 25 °C using a universal testing machine (INSTRON 5569) according to the GB/T 1040–2006 standard. Before testing, the thickness of the pristine and treated polyimide films was measured using a thickness gauge to calculate the cross-sectional area, in order to prevent the influence of creep effect during the irradiation process. The strain rate was set to 3 mm/min. The tensile strength and elongation were determined by the maximum stress and the strain, respectively; and the average values were calculated from the stress-strain curves for five samples.

3. Results and discussion

X-ray diffraction patterns of the pristine polyimide films are presented in Fig. 3, in which the films show semi-crystalline characteristics. There are three Bragg's peaks at 5.8°, 18.2°, and 25.3°, which could be indexed as (002), (110), and (210) of the polyimide, respectively [29,30]. According to previous works, the polyimide derived from PMDA and ODA would tend to form orthorhombic crystals with the space group of *Pda2* [31]. The results indicate that the polymer chains in the pristine polyimide sample are regularly ordered to some extent. When the polyimide sample is irradiated with the electron beam with a total fluence of $1 \times 10^{16}\,\mathrm{cm}^{-2}$, the