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Tensile stress effect on the macromolecular orientation and erosion mechanism of an atomic oxygen irradiated polyimide

R. Verker [a,*], N. Atar [a], F. Quero [b], S.J. Eichhorn [c], E. Grossman [a]

[a] Space Environment Department, Soreq NRC, Yavne 81800, Israel
[b] University of Manchester, Material Sciences Centre, Manchester, UK
[c] University of Exeter, College of Engineering, Mathematics & Physical Sciences, Exeter, UK

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ABSTRACT

Polyimides (PIs), used in satellites, are exposed to atomic oxygen (AO) irradiation and subjected to hypervelocity debris impacts which form residual tensile stresses and accelerated erosion.

The objectives of this work are to study the PI's macromolecular structure and its deformation and erosion mechanisms when subjected to tensile stresses in an AO environment.

The study shows that commercial PI is anisotropic, characterized by two main axis which are related to its semicrystalline structure. Under combined effects of stress and AO irradiation the PI's morphology was dependent on the direction of the applied stress and its magnitude. When the stress was applied parallel to the first main axis a carpet-like texture was formed. When the stress was however applied parallel to the second main axis an ordered surface was formed orthogonal to the direction of the applied stress.

A mechanism which relates these findings to the PI macromolecular orientation is suggested.

1. Introduction

Polyimides (PIs) are a class of thermally stable polymers that are often based on a stiff aromatic backbone which makes them infusible and insoluble. PIs possess outstanding key properties such as thermo-oxidative stability, high mechanical strength, high modulus of elasticity, high dielectric strength and superior chemical resistance [1]. PI's macroscopic properties are strongly related to their microstructural organization. In the case of Pyromellitic Dianhydride-Oxydianiline (PMDA-ODA) PI, Wide angle X-ray scattering (WAXS) studies have shown that the PMDA-ODA molecules obtain a high degree of molecular organization when orientation is induced by the presence of a substrate or by mechanical deformation [2]. Such orientation can be found in commercial PMDA-ODA PI (Kapton) which exhibits significant anisotropy in the in-plane mechanical properties, expansion coefficients and shrinkage due to stress relaxation. In a given film, maximum strength, maximum modulus and minimum ultimate elongation were found along one direction, the direction of the principal polymer chain orientation [3]. In another work, PMDA-ODA PI was uniaxially drawn during thermal curing, and the generated in-plane birefringence (Δn) was examined in relation to the molecular structure and elongation behavior. The results of these measurements showed that the magnitude of the birefringence is related to the film elongation after the completion of thermal curing [4].

In space PMDA-ODA PI is used for thermal blankets in satellites due to its durability in the space environment and unique thermo-optical properties [5]. As such, PI is exposed to the various constituents of the low Earth orbit (LEO), ranging from 200 to 1000 km [6,7], and especially to atomic oxygen (AO) irradiation and subjected to hypervelocity debris impacts.

AO, produced by the photo-dissociation of molecular oxygen in the upper atmosphere, is the main constituent of the residual atmosphere in LEO environment [8]. AO is considered as one of the most serious hazards to spacecraft external materials. Although the oxygen atoms have low density ($\sim 1 \times 10^8$ atoms/cm^3) and low energy (~ 0.04 eV), their collision with the external surfaces of a spacecraft, orbiting at a velocity of 8 km/s, results in impacts equivalent to an energy of ~ 5 eV and fluxes of 10^{14}–10^{15} O-atoms/(cm^2 s) [9].

Hypervelocity debris at LEO altitudes are man-made constituents [9,10]. Typical velocities of debris particles range from a few kilometers per second up to 16 km/s, making these hypervelocity particles a threat to spacecraft [11,12]. Ground based experiments showed that due to these impacts, residual tensile stresses are

* Corresponding author. Tel.: +972 8 943 4397; fax: +972 8 943 4403.
E-mail address: rverker@soreq.gov.il (R. Verker).

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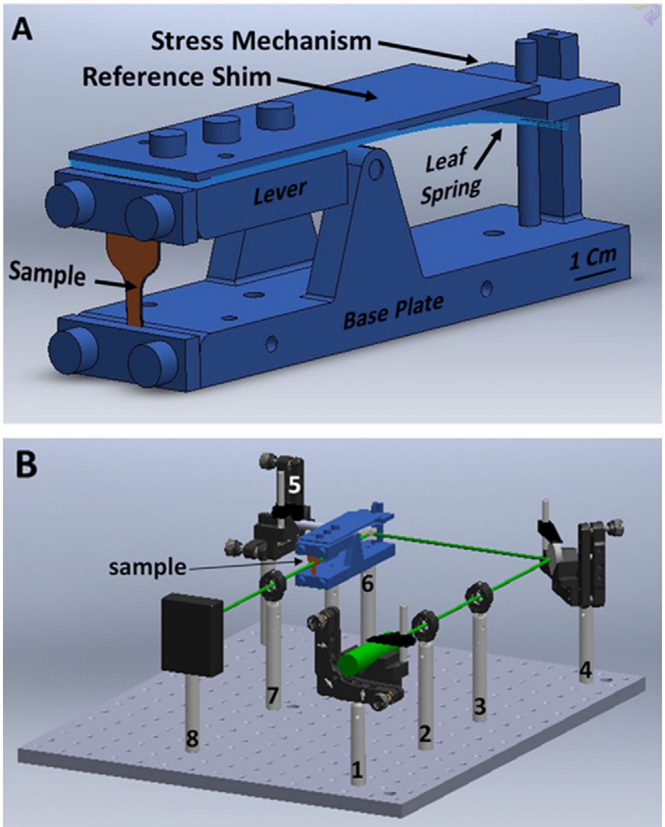

Fig. 1. Schematics of the tension-device designed for optical measurements and AO irradiation of films under tensile-stress conditions (A). Schematics of the setup used for measurements of birefringence polarimetry and DOP of the Kapton film under stress (B).

formed in PI causing accelerated erosion in an AO environment [13].

Shimamura et al. [14], exposed stressed PI films both in LEO and in ground-based simulation systems. The samples were stressed to a maximum of 7 MPa, which is in the elastic region of the PI stress–strain curve, below the yield stress [15]. According to their work, the combined effect of stress and AO irradiation did not affect the PI mechanical properties [14].

In previous work performed by Verker et al. [16], PI was locally stressed up to 100 MPa and exposed to a simulated AO environment. As a result of this exposure the PI roughness increased. The increased roughness is a result of a combined effect of stress and AO irradiation [16]. The mechanism which caused this combined effect is based on an increase in the polymer's local free volume (i.e., the volume that is not occupied by the polymer chains) in regions of higher residual tensile stress [17]. As a result, an increased oxygen diffusion into the polymer occurs [18,19] which leads to an increase in the AO-induced erosion rate [16].

However, during these previous experiments the magnitude and angle of the applied stress were not well controlled in respect to the polymer's principle chain direction.

The objective of this work is to perform a mechanochemical study regarding the erosion mechanism of PI films, which are subjected to a controlled magnitude of stress while taking into consideration the angle of the applied stress in respect to the PI chains' principle orientation direction. Mechanochemistry is associated with the mechanical activation of covalent bonds, and since force is directional, mechanical bond activation is selective [20]. The individual and combined effects of the tensile stress' magnitude (elastic and plastic) and direction, and AO fluence on the PI erosion pattern are studied in terms of changes in the surface morphology. The effect of stress magnitude on the PI's chains orientation is studied by means of Raman spectroscopy, birefringence and polarization measurements. The effect of stress magnitude and direction on the PI's mechanical properties is studied by tensile testing. Finally, a mechanism is suggested, which relates the erosion pattern by AO to the change in the PI macromolecular orientation due to stress (both direction and magnitude).

2. Experimental

The material studied in this work is a commercial PMDA-ODA PI in the form of a 25 μm-thick film, known commercially as Kapton-HN (DuPont, Inc.). The Kapton samples were die cut into dog bone-shaped samples with a constant width of 4 mm in the gauge region. Kapton film is a semicrystalline polymer characterized by anisotropic mechanical and optical properties. The film's anisotropy is attributed to a higher degree of orientation formed as a result of the machine's drawing direction during the manufacturing process. Due to this orientation the Kapton film has a diversity of about 30% in its ultimate tensile stress, while stress is applied parallel or perpendicular to its principal orientation direction [3].

The experimental work was based on a novel small tension-device which was designed for 3 tasks: (i) basic tensile stress tests (ii) birefringence and polarization measurements of Kapton samples subjected to tensile stress conditions, and (iii) AO irradiation of Kapton samples while subjected to controlled amounts of tensile stress. This device was therefore designed to fit both in an optical setup and to operate in a vacuum chamber as small as 70 mm in diameter. Within this device, see Fig. 1A, which is based on the lever principle, the Kapton sample is clamped on one side between a lever and a base plate. On the other side of the device a mechanism bends a calibrated leaf-spring that has a known spring-constant. The bend of the leaf-spring defines the force exerted on the sample. The exerted force divided by the sample's cross-section area defines the applied stress. The device was designed to take a maximum stress of 200 MPa, a stress above the Kapton's ultimate tensile strength.

Since Kapton is characterized by anisotropic mechanical properties [3], its principle orientation direction must be identified. The stress-AO irradiation experiments must take into consideration the angle between the Kapton's principle orientation direction and the direction of the stress which is applied on the sample.

The Kapton's anisotropy is expressed not only by mechanical characteristics but also by an optical anisotropy known as birefringence. Namely, the Kapton film is characterized by two unequal indices of refraction (n_1, n_2) along two principle optical axes. This optical phenomenon was used to determine the exact principle mechanical orientation of the Kapton molecular chains [3]. The optical axes were determined by a birefringence polarimetry measurements and the mechanical orientation direction was identified correspondingly.

Birefringence causes the light traveling along one axis to experience a different refractive index than light traveling along the other axis. It is possible to refer light polarized at any other direction as a combination of its projections on the two principle optical axes. The measurement presented in this work is based on the fact that when a linearly polarized light beam enters an optically anisotropic sample, the birefringence of the sample produces a relative phase shift, known as optical retardation, between the two polarization components related to the different optical axes. This phase shift along the path inside the sample is expressed by a change in the polarization orientation, which can be measured [21].