Degradation Mechanism of Polyimide Film Irradiated by Gamma Rays

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Abstract. The Co-60 radiation ground simulation test was conducted on the Mechanical property of polyimide film, thermo gravimetric and XPS was used to analyze the evolution mechanism of polyimide film in different dosages. It was found that the mechanical properties such as tensile force, tensile strength and rupture elongation of polyimide film in gamma ray radiation increase firstly and then exponent decrease. The corresponding initial decomposition temperature of the gamma ray-radiated polyimide film changed from 570°C to 590°C for weight-loss ratio of 2%. From XPS analysis, it can be found that there were rupture and crosslink of chemical bond in polyimide film. In early stage of gamma ray radiation, the rupture of C-N bond and following crosslink is for the increase of mechanical properties of polyimide film, and as the increase of radiation, the rupture of C=O and –N(CO) bond, formation of C-N bond, release of N was for the decrease of mechanical properties of polyimide films.

1. Introduction
Thin film materials have been widely used in spacecraft, especially as spacecraft thermal control materials and large-scale light materials. However, as exposed materials, thin film materials will be irradiated by energetic particles and ultraviolet radiation, results in the damage to their chemical valence bonds and performance degradation.

A large number of ground simulation tests and flight test studies have been performed on the performance of film materials, especially polyimide film materials which widely used in spacecraft, by different space environments such as atomic oxygen, ultraviolet, energetic particles, and space debris, etc. It is considered that in low-earth orbit, atomic oxygen is the main factor that causes the performance degradation of polyimide, while electrons and protons have little influence. Except for low-Earth orbit, the space radiation environment is the main environment that influences the performance of thin-film materials. To this end, in WK Stuckey et al. [1] and James E. Ferl et al. [2-6] have studied the degradation characteristics and mechanism of the thin film by different radiation environments.

Chinese scientists have studied the mechanical properties of thin film materials by different space radiation environments [7-10], especially the polyimide films under electronic, proton, and ultraviolet radiation environments.

In this paper, the degradation of the mechanical properties of polyimide films irradiated by gamma rays will be carried out, and the microstructure damage and mechanism of the film will be further studied by means of thermogravimetry and XPS analysis.
2. Experiment
Polyimide film was used as an experimental object, and the thickness was 25 μm. The irradiation test was performed on a cobalt source irradiation test device of Beijing Normal University. The vacuum degree was atmospheric pressure, the temperature was room temperature, the dose rate was 50rad (Si) / s, and the irradiation doses were 5×10⁴rad (Si) and 1×10⁵rad (Si), 5×10⁵ rad (Si), 1×10⁶ rad (Si), and 6.2×10⁶ rad (Si).

3. Mechanical Properties
The tensile strength and elongation of polyimide films at different gamma-ray irradiation doses are shown in Table 1.

Table 1. Mechanical properties of polyimide film

| Dose / rad (Si) | tensile force / N | tensile strength / MPa | elongation /% |
|----------------|-------------------|------------------------|--------------|
| 0              | 95.82             | 255.52                 | 68.05        |
| 5×10⁴          | 98.44             | 262.51                 | 75.69        |
| 1×10⁵          | 98.32             | 262.19                 | 76.17        |
| 5×10⁵          | 96.12             | 256.32                 | 71.74        |
| 1×10⁶          | 93.44             | 249.17                 | 68.45        |
| 6.2×10⁶        | 91.93             | 244.62                 | 66.32        |

It can be known from Table 1 that the mechanical properties of the polyimide film increased at the initial stage of γ-ray irradiation, and then its mechanical properties gradually decreased with the irradiation dose.

4. Damage Mechanism
4.1. Thermo Gravimetric Analysis
Thermo gravimetric analysis of polyimide films by different gamma-ray irradiation doses was studied and the relationship between the residual weight and temperature is shown in Figure 1.

Figure 1. Thermo gravimetric analysis of PI films in different electron radiations

Taking the weight loss to 98% of the original weight as the criterion for obvious weight loss of polyimide film in thermal environment, it can be seen from Figure 1 that the unirradiated sample has significant weight loss around 570 ° C, and the weight loss temperature at which the sample irradiated...
by different gamma rays increased significantly. At a dose of $1 \times 10^5$ rad (Si), the temperature at which significant weight loss occurred could reach 590 °C, and the mass of the polyimide decreased rapidly with the temperature. There was no significant change between thermo gravimetric curves at different gamma-ray irradiation doses. This indicates that a small amount of weight loss before irradiation is due to physical or chemical adsorption on the surface, and a slight increase in weight loss temperature after irradiation mainly due to small molecule resolution caused by valence bond breakage caused by irradiation.

4.2. XPS Analysis

In order to further study the reasons for the changes in the mechanical properties of polyimide films by $\gamma$-rays, their molecular structures and chemical valence bonds will be analyzed. The molecular formula of polyimide is shown in Figure 2.

![Figure 2. Molecular structural formula of polyimide](image)

Samples with doses of 0, $5 \times 10^4$ rad (Si) and $6.2 \times 10^6$ rad (Si) were selected to analyze the chemical valence bond of element C. The functional groups and their changes are shown in Table 2.

| peak/eV | 0 | $5 \times 10^4$ rad(Si) | $6.2 \times 10^6$ rad(Si) |
|---------|---|-------------------|-------------------|
|         | Strength / area ratio | Strength / area ratio | Strength / area ratio |
|         | CPS | % | CPS | % | CPS | % |
| 284.4   | — | — | — | — | 43974.96 | 36.33 |
| 284.6   | 96477.52 | 78.89 | 77228.04 | 67.40 | — | — |
| 285     | — | — | — | — | 53411.54 | 44.12 |
| 285.6   | 6880.741 | 5.63 | 17994.29 | 15.70 | 8855.347 | 7.31 |
| 286.2   | 9184.943 | 7.51 | 8835.951 | 7.71 | 4329.675 | 3.58 |
| 288.2   | 7111.305 | 5.81 | 2486.174 | 2.17 | — | — |
| 288.5   | 2638.635 | 2.16 | 8035.653 | 7.02 | 10486.91 | 8.66 |

In Table 2, the peak position 284.4eV represents the precipitation of C element, the peak position 284.6eV represents the C (2,3,5,6) of ring 2 and ring 3, and the peak position 285eV represents a substitution reaction occurs in the C (2,3,5,6) of ring 2 and ring 3, the peak position 285.6eV represents C (1,2,3,4,5,6) of ring 1, C (1) of ring 2 and C (4) of ring 3, and the peak position 286.2eV represents C (4) of ring 2 and C (1) of ring 3, the peak position 288.2eV represents the C = O bond, and the peak position 288.2eV represents the C-N bond. From the analysis in Table 1 and Figure 9, it can be seen that in the initial stage of irradiation, the fracture and cross-linking mainly occurred in ring 1. The percentage content of C = O bonds decreased, and the percentage content of C-N bonds increased. The increase of the C element at peak position 285.6eV indicates that the C = O valence bond is broken under the action of $\gamma$-rays, and at the same time cross-links with the benzene rings in rings 2 and 3, which causing the increase of the mechanical properties of PI. Further analysis was performed on the chemical valence bond of element O and its functional groups and their changes are shown in Table 3.
Table 3. Functional group of O in polyimide before and after γ ray radiation

| Peak/eV | Strength/CPS | Area ratio/\% | Strength/CPS | Area ratio/\% | Strength/CPS | Area ratio/\% |
|---------|--------------|---------------|--------------|---------------|--------------|---------------|
| 531.8   | 48605.52     | 81.13         | 33321.9      | 50.09         | —            | —             |
| 532.0   | —            | —             | —            | —             | 23577.62     | 36.64         |
| 532.2   | —            | —             | 27435.32     | 41.24         | 20545.93     | 31.93         |
| 533.1   | 11304.21     | 18.87         | 5766.551     | 8.67          | 20218.39     | 31.43         |

In Table 3, the peak position 531.8eV represents the C=O bond, the peak position 532eV represents an OH- bond, the peak position 532.2eV represents a -N(C(O)) bond, and the peak position 533.1eV represents a C-O-C bond. From the analysis in Table 2 and Fig. 10, in the initial stage of irradiation, with the increase of γ-ray irradiation, the percentage content of C = O bond and C-O-C bond decreased, and -N(C(O)) bond was generated. This is why the mechanical properties have increased during the initial period of irradiation. As the irradiation increase, the C=O bond disappears, the percentage of C-O-C bonds increases, and at the same time, -N(C(O)) decreases, and OH ions are generated, which indicates that γ-ray irradiation caused a large number of valence bonds. Fracture, free ions are generated, which is the main reason for the decrease in mechanical properties in the later stage of irradiation.

Further analysis of the chemical valence bond of the N element, its functional groups and their changes are shown in Table 4.

In Table 4, the peak positions of 399.8 eV, 400.4 eV, and 400.8 eV represent the -N (C (O)) bond, the C-N bond, and the N element, respectively. From the analysis in Table 5 and Figure 11, it can be known that in the initial stage of irradiation, the percentage content of CN bonds increased with the γ-ray irradiation, at the same time, the percentage content of -N(C (O)) decreased. At the beginning of irradiation, the C = O bond decreases correspondingly. With the further increase of irradiation, -N(C(O)) gradually disappeared and elemental N was generated, which indicates that the valence bond breakage of the polyimide film further occurred with the γ-ray irradiation, which leads to a reduction in mechanical properties.

Table 4. Functional group of N in PI before and after electron radiation

| Dose / rad (Si) | Peak position / eV | Intensity / CPS | Area ratio /% |
|-----------------|--------------------|----------------|---------------|
| 0               | 399.8              | 6526.613       | 65.79         |
|                 | 400.4              | 3393.111       | 34.21         |
| 5×10^4          | 399.8              | 3794.17        | 27.28         |
|                 | 400.4              | 10112.75       | 72.72         |
|                 | 399.8              | —              | —             |
| 1×10^6          | 400.4              | 14461.99       | 100           |
|                 | 400.4              | 11216.89       | 72.06         |
| 6.2×10^6        | 400.8              | 4349.157       | 27.94         |

5. Conclusions

From above research, following conclusions can be obtained:

(1) The polyimide film has a total dose effect under γ-ray irradiation, and its tensile force, tensile strength, and elongation increase firstly and then decrease with the irradiation.

(2) Temperature at which polyimide film exhibits significant weight loss increase after it irradiated by γ-ray

(3) In the initial stage of γ-ray irradiation, the breakage of C-N bonds and the cross-linking induced by them are the main reasons leading to the increase of mechanical properties of polyimide film.
(4) The break of the C = O double bond and the -N (CO) bond, the formation of new C-N bond and the precipitation of N element are the main reasons to the decrease of the mechanical properties of polyimide with the $\gamma$-ray irradiation.

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7. References
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