Degradation and Mechanism of Mechanical Properties of Polyimide Film Irradiated by Gamma Ray

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Abstract. Polyimide (PI) films might be damaged under space high energy particle irradiation. In this paper, the mechanical properties and mechanism of polyimide film is studied with the ^{60}Co radiation source, the thermo-gravimetric analysis and the XPS analysis. Significant total dose effect is found in the mechanical properties of the PI film under gamma ray radiation. The tensile strength and rupture elongation of polyimide film increase first and then decrease exponentially with the increase of irradiation dose. 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 are widely used in spacecraft thermal control structures and inflatable structures such as solar sails. Due to long-term exposure to the surface of spacecraft, affected by various spatial environmental effects, its mechanical properties may be degraded due to the harsh environment of space.

The corrosion rate and mechanical properties of POSS polyimide film under the synergistic effect of atomic oxygen and space debris were studied by R. Verker [1]. The degradation of mechanical properties of polyimide film under space flight test environment is studied by Hiroyuki Shimamura [2]. It is considered that atomic oxygen is the main factor leading to the decrease of its performance, while electron and ultraviolet have little influence on its performance. Joyce A. Dever [3] had studied the mechanical properties of the Teflon FEP used in Hubble Space Telescope and found that its mechanical properties degraded with the increase of irradiation time. Besides, many scientists had given attention on the degradation mechanism of thin films under different radiation conditions [4-9].

In this paper, ^{60}Co is used to test the mechanical properties of polyimide film used in the radiation environment of high-energy particles; furthermore, the degradation mechanism of it is discussed.

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2. Test scheme

2.1. Sample preparation
The test samples are PI film, and its thickness is 25μm, besides samples used in proton irradiation is 50μm. It was cut into special sample with 150mm length and 15mm width, and the edge of sample must smooth and without any small gap.

2.2. Test parameters
The test samples irradiated by ^{60}Co ray. The radiation dose rate is 50rad (Si) /s, and the total dose is 5×10^4rad(Si),1×10^5rad(Si), 5×10^5rad(Si), 1×10^6rad(Si)and 6.2×10^6rad(Si)respectively.

3. Mechanical property analysis
The rupture elongation and tensile strength of PI films radiated by ^{60}Co gamma ray are illustrated in Fig.1, Fig.2 and Fig.3.

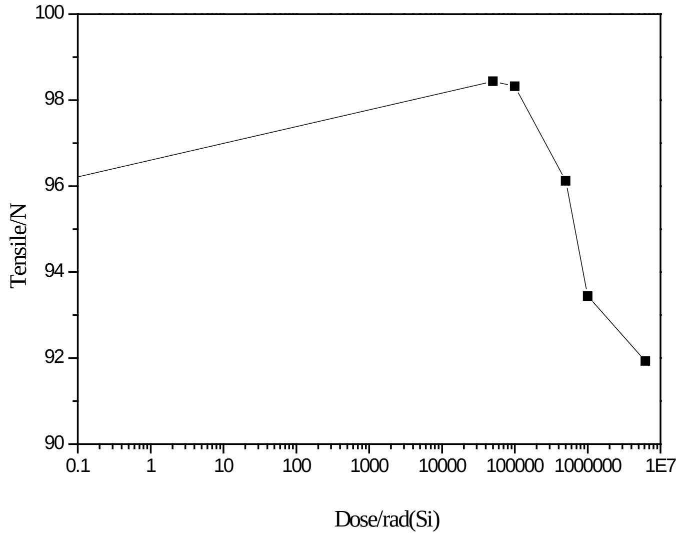

Figure 1. Tensile of polyimide in different γ ray dosages

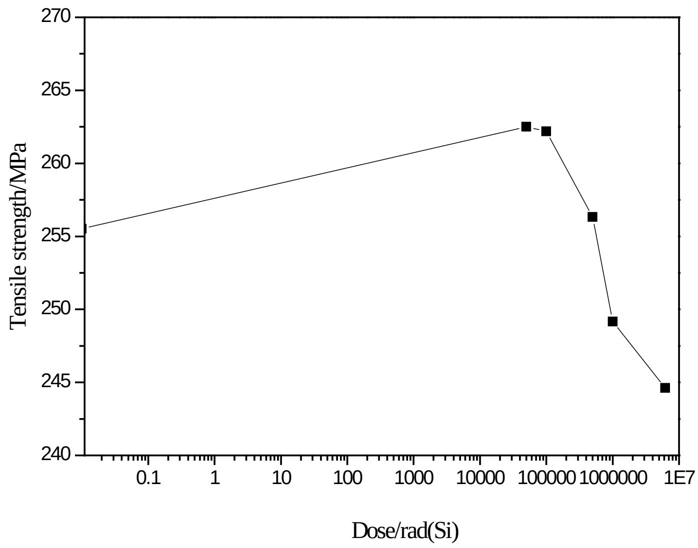

Figure 2. Tensile strength of polyimide in different γ ray dosages

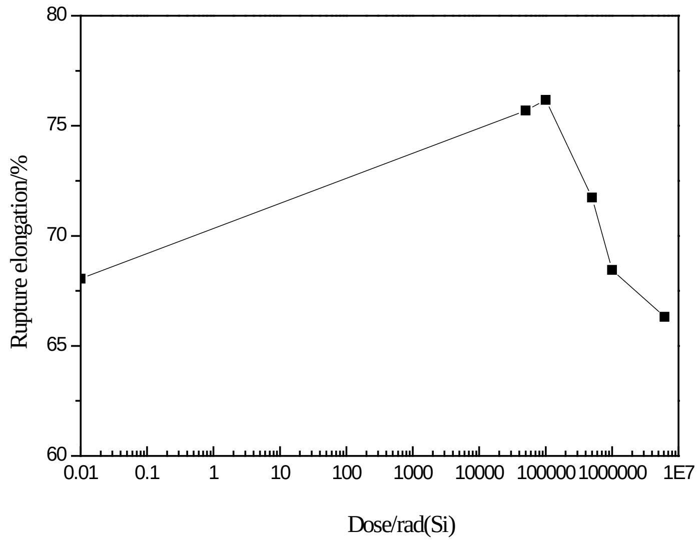

Figure 3. Rupture elongation of polyimide in different γ ray dosages

From Fig. 1, Fig. 2 and Fig. 3, it can be seen that the mechanical properties of polyimide film increase firstly andthen gradually decrease with the increase of irradiation dose.

The relation between tensile and radiation dose was fitted as Figure4.

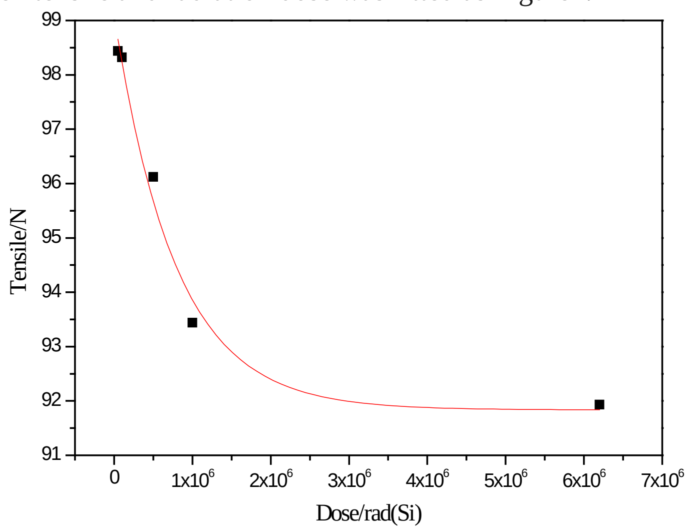

Figure 4. Fitting curve of Kapton tensile in different gamma ray doses

After radiation of 5×10^4 rad(Si) gamma ray, the tensile of polyimide film decreases exponentially with the increase of radiation dose, and finally tends to stabilize.

The degradation of tensile of polyimide film as the function of

$$y = 91.835 + 7.268\exp(-x/782354.479) \quad (x>50000) \tag{1}$$

Here, y is tensile, N; x is dose, rad(Si).

The relation between tensile strength and radiation dose was fitted as Figure5.

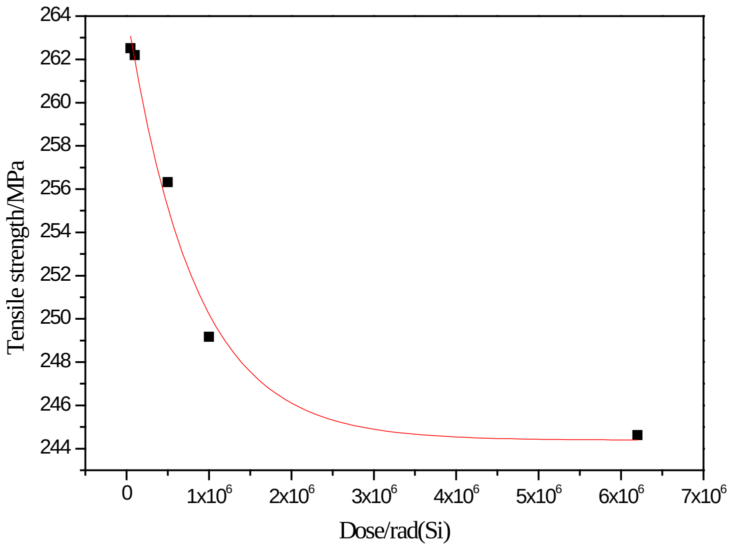

Figure 5. Fitting curve of PI tensile strength in different γ ray dosages

After radiation of 5 * 10^4 rad(Si) gamma ray, the tensile of polyimide film decreases exponentially with the increase of radiation dose, and finally tends to stabilize.

The degradation of tensile of polyimide film as the function of

$$y = 244.391 + 19.857\exp(-x/816643.640) \quad (x>50000) \tag{2}$$

Here, y is tensile strength, MPa; x is dose, rad(Si).

The relation between rupture elongation and radiation dose was fitted as Figure6.

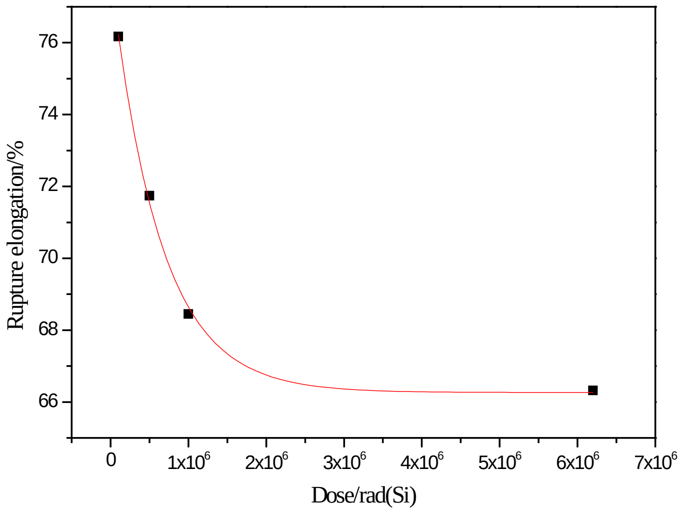

Figure 6. Fitting curve of Kapton rupture elongation in different γ ray dosages

After radiation of 1 * 10^5 rad(Si) gamma ray, the rupture elongation of polyimide film decreases exponentially with the increase of radiation dose, and finally tends to stabilize.

The degradation of tensile of polyimide film as the function of

$$y = 66.264 + 11.682\exp(-x/629077.636) \quad (x>1\times10^5) \tag{3}$$

Here, y is rupture elongation, %; x is dose, rad(Si).

4. Mechanism research

4.1. Thermogravimetric analysis

The thermogravimetric analysis of polyimide films at different doses of gamma ray irradiation was carried out. The relationship between the percentage of residual weight and temperature was shown in Figure 7.

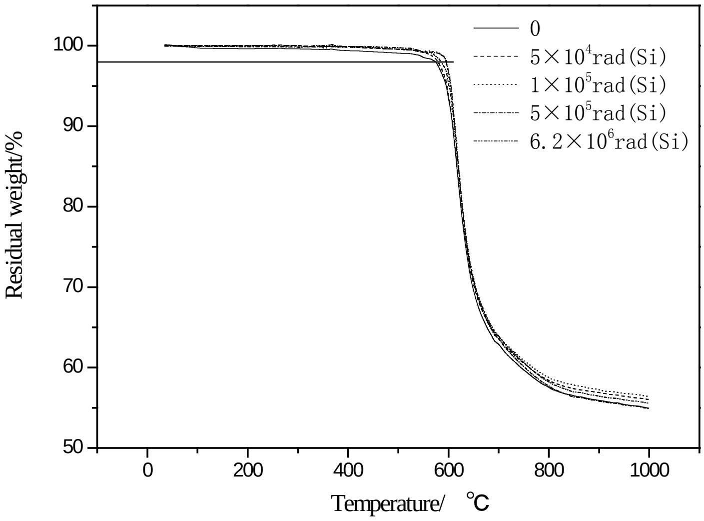

Figure 7. Thermo gravimetric analysis of PI films in different electron radiations

98% of weight loss to the original weight is used as the criterion of apparent weight loss. From the film thermo-gravimetric analysis curves, it show that the weightlessness of unirradiated samples appeared at around 570°, and the obvious weight loss temperature increased significantly after the samples are radiated by ^{60}Co ray. When the dose is 1×10^{5}rad (Si), the weightlessness temperature up to 590° .

4.2. XPS analysis

In order to further study the change of mechanical properties of polyimide film under the action of gamma ray, the molecular structure and chemical valence bond of polyimide film were analysed. The molecular formula of polyimide is shown in Figure 8. [14]

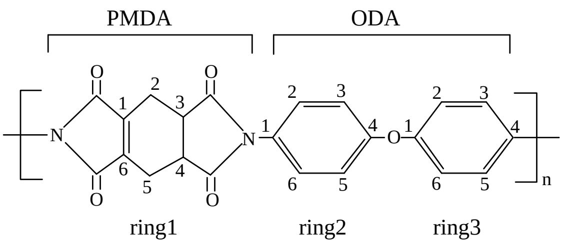

Figure 8. Molecular structural formula of polyimide

The chemical valence bonds of C, O, N elements of polyimide with radiation dose in 0, 5 × 104 rad (Si) and 6.2 × 10^{6}rad (Si) were analyzed as shown in Table 1 to Table 3.

In Table 1, the peak of 284.4eV is C, the peak of 284.6eV and 285eV represents C (2,3,5,6) of ring2 and ring3, the peak 285.6eV represents the C ring (1,2,3,4,5,6) of ring1, C (1) of ring2 and C (4) a of ring 3, the peak of 286.2eV is C (4) of ring2 and C (1) of ring3, the peak of 288.2eV is C=O, and peak of 288.2eV is C-N.

Table 1. Functional group of C in PI before and after electron radiation

energy/eV	0		5×10^4 rad(Si)		6.2×10^6rad(Si)	
	intensity/CPS	area ratio /%	intensity/CPS	area ratio /%	intensity/CPS	area ratio /%
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

At the beginning of radiation, the rupture and crosslink of chemical bond of PI mainly occurred in the ring 1, and results in the decreases of C=O bond and increases of C-N bond, at the same time, there is crosslink of benzene ring in ring 2 and ring 3, which is the cause of the increase of mechanical properties of PI film. With the further action of gamma ray, valence bond rupture and cross-link occurs mainly in the ring2 and ring3, partial C-O-C bonds between ring 2 and ring 3 break, and some break also appears in ring 1, at the same time, there are the C element or the C free ion formation, resulting in decreased mechanical properties.

Table 2. Functional group of O in polyimide before and after γ ray radiation

energy/eV	0		5×10^4 rad(Si)		6.2×10^6rad(Si)	
	intensity/CPS	area ratio /%	intensity/CPS	area ratio /%	intensity/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 2, the peak of 531.8eV, 532eV, 532.2eV, 533.1eV is the C=O, OH-, -N (C (O), C-O-C separately. From tables 2, we can see that the percentage of C=O bond and C-O-C bond decreases with the increase of gamma irradiation at the initial stage of radiation, and -N (C (O)) bond is generated at the same time, which is the origin of mechanical properties increase at the initial stage. With the increase of irradiation dose, C=O bond disappeared. At the same time, -N (C (O)) decreases and OH ions are generated. This indicates that gamma irradiation causes a large number of valence bonds to break, and free ions are generated, which is the main reason for the decrease of mechanical properties in the later stage of irradiation.

In Table 3, the peaks of 399.8eV, 400.4eV, and 400.8eV represent the -N (C (O)), C-N and N element respectively. From table 3, we can see that at the initial stage of irradiation, the percentage of C-N bonds increases and the -N (C (O)) decreases with the increase of gamma irradiation, which is corresponding to the decrease of C=O bond in the O element at the initial stage of irradiation. With the increase of dose, -N (C (O)) disappears and N is formed. This indicates that with the further increase of gamma irradiation dose, the further bond breaking of polyimide film occurs, resulting in the decrease of mechanical properties.

Table 3. Functional group of N in PI before and after electron radiation

dose/rad(Si)	energy/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
1×10^6	399.8	—	—
	400.4	14461.99	100
6.2×10^6	400.4	11216.89	72.06
	400.8	4349.157	27.94

5. Conclusions

Through the study, following conclusions can be obtained:

(1) The mechanical properties of the PI film has significant total dose effect under gamma ray radiation. The tensile strength and rupture elongation of polyimide film increase first and then decrease exponentially with the increase of irradiation dose.

(2) After be radiated by gamma ray, the temperature of apparent weight loss of the polyimide film increases.

(4) At the initial stage of gamma ray irradiation, the fracture of the C-N bond and its induced crosslink are the main reasons for the increase of the mechanical properties of PI film.

(5) With the increase of gamma dose, the breakage of C=O and -N (CO), the formation of C-N and the precipitation of N are the main reasons for the decrease of mechanical properties of PI film.

6. References

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