Comparison of damage mechanism of polyimide films in space radiation environments

Z C Shen1,*, Y G Ding1, Y Z Wang2 and H B He2

1Beijing Institute of Spacecraft Environment Engineering, No.104, Youyi Road, Haidian District, Beijing100094, China
2Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, No.390,Qinghe Road, Jiading District, Shanghai 201800, China

Email: zicaishen@163.com

Abstract. Thin polyimide (PI) films are widely used as structure material or functional material of spacecraft, but their microstructure and properties may be damaged by space radiation environments such as electron, proton, and ultraviolet and so on. By using space combined radiation simulation facility and X ray photoelectron spectroscopy (XPS), the damage mechanism of PI film in different irradiation environments were studied. Both charged particles and ultraviolet photons cause the breakage and cross linking of molecular bonds of PI films. Among them, the charged particles mainly show that the PI film breaks the molecular valence bond, while the ultraviolet photon mainly shows the cross linking of the molecular valence bond. For charged particles, the breakage of PMDA molecular chain, especially the break of C = O double bond and -N(CO) bond is the main effect, and at the same time, C-O is generated. For UV irradiation, the breakage of C-O bond, C-O bond, C-N bond and C-C bond mainly occurred firstly, and then the cross-linking between ions of C, N, O with the benzene ring and between different benzene rings will appears with the UV irradiation.

1. Introduction

Thin films and coatings are widely used on spacecraft as inflatable deployment structures or thermal control materials. As exposed materials, their mechanical properties will be damaged by space radiation environments such as ultraviolet, electron, proton, etc.

A lot of studies on the mechanical properties of films or coatings have been done. R. Verker et al. [1] had given the study on the tensile and erosion rate of polyimide films in the space debris and atomic oxygen environment; H. Shimamura and his coworkers [2] had studied the properties of polyimide in flight environments. J. A. Dever[3] had found that the mechanical properties of Teflon film had obvious degradation with the irradiation. W.K.Stuckey et al. [4] had given a ground simulation irradiation experiments on the thin films used for the space deployment structure, and evaluated their tensiles too. J. E.Ferl and his colleagues[5-8] had studied the influence of space radiation environments on the tensile properties and damage mechanism of the film. But, there was little studies focus on the micro damage mechanism of films such as micro defect, charge transport, molecular bonds, etc [9]. In China, some researches [10-15] studied the mechanical properties of thin films or coatings in different radiation environments.

In this paper, the damage mechanism of PI films under different space radiation environments such as ultraviolet, electrons and protons will be studied and compared.
2. Experiment and test
PI films were used as samples and their thickness were 25 μm. The energy of electron irradiation was 40 keV, and the fluencies were 0, 2×10^{15} e/cm², 6×10^{15} e/cm², 1.0×10^{16} e/cm², 1.4×10^{16} e/cm² separately. The energy of proton irradiation was 45 keV, and the fluencies were 0, 1×10^{14} p/cm², 3×10^{14} p/cm², 5×10^{14} p/cm², 7×10^{14} p/cm², 10×10^{14} p/cm² separately. The mercury xenon lamp was used as NUV irradiation source and its energy was 1000 W, which can realize the acceleration factor of 4, the exposure of NUV irradiation was 0, 100 ESH, 200 ESH, 300 ESH, 500 ESH, and 1000 ESH separately. The deuterium lamp which can realize the acceleration factor of 10 was used to FUV irradiate thin films, the exposure is 0, 300 ESH, 600 ESH, and 1000 ESH separately. The background temperature of the facility was kept at -35°C. The temperature of the samples was kept at about 20°C by a thermostatical control system. The vacuum of irradiation was less than 3.0×10^{-3} Pa.

The component and binding energy of samples were studied by Eacaphi5700 X-ray photoelectron spectroscopy (XPS), AlKα with energy of 1486.6 eV is used as X-ray source.

3. Damage mechanism
PI is a organic polymer, its molecular is [(C_{22}H_{10}O_5N_2)_n] and the percent of C, O and N component in PI is 75.9%, 17.2% and 6.9% separately. The molecular constitution is illustrated in Figure 1.

![Figure 1. Molecular structural formula of PI.](image)

For C element in PI, the 284.4 eV peak and the change of its intensity illustrated that there was substitution reaction in ring 2 and ring 3, and result in the generation of the C (1,2,3,4,5,6), the 284.7 eV peak represents the C (2,5) in ring 1, the C (2, 3,5,6) in ring 2 or ring 3, the 285.6 eV peak represents the C (1) in ring 2 or the C (4) in ring 3, the 286.2 eV peak represents the C (4) in ring 2 or the C (1) in ring 3, the 288 eV peak and the 288.2 eV peak represent the C = O bond, the 288.5 eV peak represents the C-N bond.

For O element in PI, the 531.6 eV peak or the 531.8 eV peak represents the C = O bond, the 532.2 eV peak or the 532.5 eV peak represents the -N (C (O)) bond, and the 533.1 eV peak represents the C-O-C bond.

For N element in PI, the 399.81 eV peak represents the -N (C (O)) bond, the 400.4 eV peak represents the C-N bond, and the 400.8 eV peak represents the N element.

3.1. NUV irradiation
Percentage of component such as C, N, O in PI film before and after NUV irradiation was analyzed by XPS and listed in Table 1.

| NUV irradiation /ESH | C/%  | O/%  | N/%  |
|---------------------|------|------|------|
| 0                   | 79.75| 15.18| 5.07 |
| 100                 | 55.91| 39.07| 5.02 |
| 300                 | 59.47| 32.73| 7.8  |
| 500                 | 58.17| 34.15| 7.68 |
| 1000                | 59.91| 33.20| 6.89 |
It can be seen from Table 1 that the C in PI films decreases firstly, and then increases with NUV irradiation, but the N and O increases firstly and then decreases.

Bind energy change of C1s, N1s and O1s in PI by NUV irradiation is listed in Table 2.

### Table 2. Functional group in PI irradiated by NUV

| Component | Peak/eV | Before irradiation | 300ESH | 1000ESH |
|-----------|---------|--------------------|--------|---------|
|           | Intensity/CP S | Percent/ | Intensity/CP S | Percent/ | Intensity/CP S | Percent/ |
| C         |          |                    |        |         |          |        |         |
| 284.4     |          | 74966.48           | 71.20  | 77488.21| 75.33   |
| 284.7     | 76423.59 | 74.64              |        |         |         |
| 285.6     | 7315.697 | 7.15               | 19110.88| 18.15  | 15880.8 | 15.44  |
| 286.2     | 9176.194 | 8.96               |        |         |         |
| 288       |          | 11212.89           | 10.65  | 9496.055| 9.23    |
| 288.2     | 3312.523 | 3.24               |        |         |         |
| 288.5     | 6159.39  | 6.01               |        |         |         |
| 531.6     |          | 46881.12           | 70.45  | 44628.19| 70.81   |
| 531.8     | 38632.45 | 71.17              |        |         |         |
| 532.5     |          | 9106.628           | 13.69  | 10286.18| 16.32   |
| 533.1     | 15647.97 | 28.83              | 10556.61| 15.86  | 8113.907| 12.87  |
| N         | 399.81   | 2449.84            | 18.32  | 13827.15| 15.86   |
| 400.4     | 10924.78 | 81.68              | 3324.005| 19.38  | 248.3543| 0.19   |

From Table 2, the C-C bond, C-N bond and C-O bond will break at the early stage of NUV irradiation. With the NUV irradiation, the C = O bond will cross-link with the benzene ring, and the C-O bond and the C-N bond will disappear.

#### 3.2. FUV irradiation

Percentage of component such as C, N, and O in PI film before and after FUV irradiation was analyzed by XPS and listed in Table 3.

| Component | FUV exposure /ESH | C/% | O/% | N/% |
|-----------|------------------|-----|-----|-----|
| 0         | 79.75            | 15.18| 5.07|
| 300       | 75.56            | 18.90| 5.54|
| 500       | 77.51            | 19.45| 3.04|
| 800       | 77.68            | 18.43| 3.89|
| 1000      | 78.66            | 17.62| 3.72|

From Table 3, the N and O in PI increases firstly and then decreases with FUV irradiation, on the contrary, the C in PI decreases firstly and then increases with FUV irradiation.

Bind energy change of C1s, N1s and O1s in PI by FUV irradiation is listed in Table 4.

From Table 4, the broke of the C-O-C in PI film appears firstly and the rupture is the main effect, which results in the increase of C=O and the cross-link which results in the increase of C-O-N bond and the decrease of C-O-C bond. The decrease of the C = O bond is attributed to the breakage of C-O-C bond and C-N bond, the cross-link of the C (1) in ring 3 and the C (4) in ring 2, and results in the C (2,3, 5,6) increases.

#### 3.3. Electron irradiation

Percentage of component such as C, N, O in PI film before and after electron irradiation was analyzed by XPS and listed in Table 5.
Table 4. Functional group in PI irradiated by FUV

| Component | Peak/eV | Before irradiation | 300ESH | 1000ESH |
|-----------|--------|--------------------|--------|--------|
|           |        | Intensity/CP S | %      | Intensity/CP S | %      | Intensity/CP S | %      |
| C         | 284.4  | —              | —      | 11859.28  | 11.79  | 13329.22  | 14.57  |
|           | 284.7  | 76423.59       | 74.64  | 42950.69  | 42.71  | 23071.94  | 25.22  |
|           | 285.6  | 7315.697       | 7.15   | 34240.91  | 34.05  | 44327.03  | 48.46  |
|           | 286.2  | 9176.194       | 8.96   | —         | —      | —         | —      |
|           | 288.2  | 3312.523       | 3.24   | —         | —      | —         | —      |
|           | 288.5  | 6159.39        | 6.01   | 11520.15  | 11.45  | 10750.45  | 11.75  |
| O         | 531.8  | 38632.45       | 71.17  | 13514.58  | 21.06  | 23715.47  | 36.33  |
|           | 532.2  | 41509.86       | 64.69  | 19280.24  | 34.14  |
|           | 533.1  | 15647.97       | 28.83  | 9144.681  | 14.25  |
|           | 399.81 | 2449.84        | 18.32  | 1392.982  | 10.09  | 2698.966  | 23.34  |
| N         | 400.4  | 10924.78       | 81.68  | 8581.198  | 14.25  | 3913.804  | 23.34  |
|           | 400.8  | —              | —      | 3826.958  | 27.73  | 4952.307  | 42.82  |

From Table 5, the percentage of C element and N element decreases while the content of O element increases with electron irradiation.

Table 5. Percentage of material component irradiated by electron

| Fluence/10¹⁵ e/cm² | C/%  | O/%  | N/%  |
|---------------------|------|------|------|
| 0                   | 79.75| 15.18| 5.07 |
| 1                   | 78.17| 17.12| 4.71 |
| 3                   | 77.49| 17.75| 4.76 |
| 5                   | 78.4 | 17.05| 4.55 |
| 10                  | 77.67| 17.72| 4.605|

From Table 5, the percentage of C element and N element decreases while the content of O element increases with electron irradiation.

Bind energy change of Cls, N1s and O1s in PI irradiated by electron is listed in Table 6.

Table 6. Functional group of PI irradiated by electron

| Component | Peak/eV | Before irradiation | 1×10¹⁵ e/cm² | 10×10¹⁵ e/cm² |
|-----------|--------|--------------------|--------------|---------------|
|           |        | Intensity/CP S | %      | Intensity/CP S | %      | Intensity/CP S | %      | Intensity/CP S | %      |
| C         | 284.7  | 76423.59       | 74.64  | 76728.78  | 77.62  | 46831.4  | 51.75  |
|           | 285    | —              | —      | —         | —      | 21205.47 | 23.43  |
|           | 285.6  | 7315.697       | 7.15   | 2058.22   | 2.08   | 8031.59  | 8.88   |
|           | 286.2  | 9176.194       | 8.96   | 12246.18  | 12.39  | 6997.907 | 7.73   |
|           | 288.2  | 3312.523       | 3.24   | 3740.22   | 3.79   | —        | —      |
|           | 288.5  | 6159.39        | 6.01   | 4075.29   | 4.12   | 7429.286 | 8.21   |
|           | 531.8  | 38632.45       | 71.17  | 40057.12  | 72.44  | —        | —      |
| O         | 532.0  | —              | —      | —         | —      | 41852.14 | 73.11  |
|           | 532.2  | —              | —      | 3528.582  | 6.38   | —        | —      |
|           | 533.1  | 15647.97       | 28.83  | 11713.54  | 21.18  | 15390.62 | 26.89  |
|           | 399.81 | 2449.84        | 18.32  | 5184.02   | 55.75  | —        | —      |
| N         | 400.4  | 10924.78       | 81.68  | 4114.47   | 44.25  | 9267.05  | 94.18  |
|           | 400.8  | —              | —      | —         | —      | 572.79   | 5.82   |

From Table 6, the fracture and cross-link of ring 1 mainly occurred in the early electron irradiation, there is the fracture of C-N. With the electron irradiation, the C-N bonds increases, the bond of the C =
O and the C-O decreases, and the bond of C = O disappears, and the bond of C-O-C decreases firstly and then increases with irradiation. When the electron irradiation was performed, the C-O bond is broken, and then the O ion participates in the crosslinking, which is consistent with the change of the C-O and the C = O bonds in the C element. Under electron irradiation, the PI film first breaks the molecular valence bond, resulting in O enrichment on the surface, and the N element may be due to the generation of N ions or N elements, which is resolved from the surface.

3.4. Proton irradiation

Percentage of component such as C, N, O in PI film before and after proton radiation was analyzed by XPS and listed in Table 7.

| Component | Peak/eV | Intensity/CPS | Percent/% | After irradiation | Intensity/CPS | Percent/% |
|-----------|---------|---------------|------------|------------------|---------------|------------|
| C         | 284.7   | 50326.68      | 44.76      | 22372.17         | 16.03         |
|           | 285.0   | -             | -          | 37590.60         | 26.93         |
|           | 285.6   | 41058.55      | 36.52      | 45709.01         | 32.75         |
|           | 286.2   | 9020.808      | 8.02       | 22720.52         | 16.28         |
|           | 288.2   | 6099.284      | 5.42       | 3050.22          | 2.19          |
|           | 289.0   | 5927.26       | 5.28       | 8123.20          | 5.82          |
|           | 532.2   | 50240.13      | 62.80      | 36948.87         | 41.24         |
|           | 532.8   | 16492.77      | 20.62      | 38918.99         | 43.44         |
|           | 533.8   | 13264.7       | 16.58      | 13723.39         | 15.32         |
|           | 399.8   | 1132.854      | 12.77      | 1525.672         | 14.29         |
|           | 400.8   | 7735.03       | 87.23      | 9154.058         | 85.71         |

From Table 7, it can be seen that C increases, while O and N decreases after proton radiation.

Bind energy change of C1s, N1s and O1s in PI before and after proton radiation is listed in Table 8.

| Component | Peak/eV | Intensity/CPS | Percent/% | After irradiation | Intensity/CPS | Percent/% |
|-----------|---------|---------------|------------|------------------|---------------|------------|
| C         | 284.7   | 50326.68      | 44.76      | 22372.17         | 16.03         |
|           | 285.0   | -             | -          | 37590.60         | 26.93         |
|           | 285.6   | 41058.55      | 36.52      | 45709.01         | 32.75         |
|           | 286.2   | 9020.808      | 8.02       | 22720.52         | 16.28         |
|           | 288.2   | 6099.284      | 5.42       | 3050.22          | 2.19          |
|           | 289.0   | 5927.26       | 5.28       | 8123.20          | 5.82          |
|           | 532.2   | 50240.13      | 62.80      | 36948.87         | 41.24         |
|           | 532.8   | 16492.77      | 20.62      | 38918.99         | 43.44         |
|           | 533.8   | 13264.7       | 16.58      | 13723.39         | 15.32         |
|           | 399.8   | 1132.854      | 12.77      | 1525.672         | 14.29         |
|           | 400.8   | 7735.03       | 87.23      | 9154.058         | 85.71         |

From Table 8, the functional group and percentage of PI film changed after irradiated by proton, and there is rupture of C=O, increase of C-O, oxidation of N, and appearance of C-OH and OC(O)N bond. There is chemical effect between proton and PI film, and rupture and linkage cross of molecular chain occurs. During proton irradiation, rupture and linkage cross appears at the same time, but rupture is the main chemical effect.

4. Conclusions
Following conclusions can be obtained:

(1) Both charged particles and ultraviolet photons cause the breakage and crosslinking of molecular bonds of PI films. Among them, the charged particles mainly show that the PI film breaks the molecular valence bond, while the ultraviolet photon mainly shows the crosslinking of the molecular valence bond.

(2) Under the action of electrons or protons, the PI film undergoes C-N bond rupture and new C-N bond formation. With the increase of irradiation fluence, the breakage of PMDA molecular chain,
especially the break of the -N (CO) bond and the C = O bond is the main cause, and the C-O bond is generated too.

(3) In the initial UV irradiation, the C-O bond was broken, then some bonds such as the C = O, the C-N and the C-C was generated. With the UV irradiation, the ions of C, N, and O interact with the benzene ring and cross-linking reaction will occur, and the bond of C-O and C-N will disappear.

Acknowledgments
This work supported by National Key R&D Program of China (No.2018YFE0118000), National Natural Science Foundation of China (No.11975052) and National key program (No. JSHS2016203A001).

References
[1] Verker R, Grossman E and Eliaz N 2009 Acta Materialia 57 1112
[2] Shimamura H and Yamagata I 2009 J. spacecraft rockets 46 15
[3] Joyce A D, Kim K G and Jacqueline A T 1998 AIAA 0895 1
[4] Stuckey W K, Meshishnek M J and Hanna W D 1998 Aerospace Report TR-98(1055)-1 1
[5] Albarado T L, Hollerman W A and Edwards D 2005 J. Solar Energy Engineering 127 125
[6] Dennis A R, John W C and Lawrence B F 2001 AIAA 1414 1
[7] David E, Whitney H and Tesia S 2002 SPIE 4823 67
[8] David E, Charles S and Mary H 2004 SPIE 5554 80
[9] Elena A P, Daniel P E and Russell C 2018 J. Vacu. Scie. Tech. B 36 052906
[10] Shen Z C, Zheng H Q and Zhao X 2010 Spacraft Environ. Eng. 27 600
[11] Zhang F, Shen Z C and Feng W Q 2012 Spacraft Environ. Eng. 29 315
[12] Huang X Q, Wang L and Liu Y F 2014 Vacuum and Cryogenics 20 154
[13] Shen Z C, Mu Y Q and Wu Y Y 2015 Equip. Environ. Eng. 12 42
[14] Shen Z C, Guo L and Ma Z L 2016 Spacraft Environ. Eng. 33 100
[15] Shen Z C, Qiu X L, Mu Y Q 2017 Vacuum & Cryogenics 23 82