Mechanical Property Evolution Model of Polyimide Film by Far Ultraviolet Irradiation

Zicai Shen, Yan Xia, Chunqing Zhao, Yigang Ding, Peng Fan and Jian Li
Beijing Institute of Spacecraft Environment Engineering, No.104, Youyi Road, Haidian District, Beijing, China(100094)
Email: zicaishen@163.com

Abstract. The deuterium lamp was used as simulation source to study the Mechanical property of polyimide film in space far ultraviolet environment, thermo gravimetric and XPS was used to analyze the evolution mechanism of polyimide film in different exposures. It was found that the mechanical properties such as tensile strength and rupture elongation of polyimide film decrease firstly and then exponent increase until to stable. From XPS analysis, it can be found that there were rupture and crosslink of chemical bond in polyimide film. In early stage of far ultraviolet radiation, the rupture of C-N, C=O, C-O, C-C bond is for the decrease of mechanical properties of polyimide film, and as the increase of far ultraviolet exposure, the release of N, and formation of C-N bond is for the increase of mechanical properties of polyimide film.

1. Introduction
Thin film materials are widely used as thermal control structures and inflatable deployment structures of spacecraft. Due to the long-term exposure to the space environments such as electron, proton, ultraviolet and so on, the structure of the thin film materials may be damaged and results in the degradation of their mechanical properties.

A lot of researches have been done on the mechanical properties of aerospace film materials. R. Verker et al. [1] studied the erosion rate and mechanical properties of POSS polyimide films under the synergistic effect of atomic oxygen and space debris environment; Hiroyuki Shimamura et al. [2] studied polyimide under space flight test environment. Joyce A. Dever et al. [3] found that with the increase of irradiation time, the mechanical properties of Teflon FEP secondary surface mirror films for the Hubble Space Telescope had obvious degradation. W.K.Stuckey et al. [4] conducted ground simulation experiments on the space radiation environmental effects of thin film materials for inflatable deployment structures, and evaluated their mechanical properties degradation. James E.Ferl et al. [5-8] also studied the degradation of the mechanical properties and microscopic mechanism of the film under different radiation environments. Zhang Fan and many other Chinese researches [9-12] also studied the mechanical properties of thin film materials under the radiation environments such as electrons, protons and ultraviolet.

Based on the damage mechanism of mechanical properties of polyimide film irradiated by far ultraviolet irradiation, a mathematical model and a physical model of mechanical properties degradation of polyimide films irradiated by far-ultraviolet radiation will be proposed in this paper to provide theoretical support for the performance degradation prediction of films in space environments.
2. Experiment
Using a special cutter, the polyimide film produced by DuPont with a thickness of 25μm was cut into a 15 mm wide and 150 mm long specimen. Examine them with a lighting magnifier and discard the specimen with defective edges.

The irradiation test was performed on the Φ800 space comprehensive irradiation simulator at Beijing Institute of Space Environment Engineering. Deuterium lamp was selected as the source of far ultraviolet radiation, the wavelength range is 115nm~200nm, the acceleration factor was 10, the sample temperature was 25°C, the vacuum degree was better than 1×10⁻³Pa, and the far ultraviolet exposure was 0ESH, 300ESH, 500ESH, 800ESH and 1600ESH. After the irradiation, the sample was taken out and the tensile test was performed with an electronic tensile testing machine. Gage length is 100mm, and stretching speed is 50mm/min.

3. Mechanical Properties
The experimental results of tensile strength and elongation of polyimide film materials under different far ultraviolet exposures are shown in Figure 1 and Figure 2 respectively.

![Figure 1. Tensile strength of PI in FUV irradiation](image1)

![Figure 2. Rupture elongation of PI in FUV irradiation](image2)

Fitting the tensile strength after 300ESH far-ultraviolet exposure shows that the tensile strength of the film increases exponentially with the far-ultraviolet exposure:

\[ y = 177.481 - 17.01 \exp \left( - \frac{x}{1445.788} \right) \quad (x>300) \]

Here, \( y \) is the tensile strength, MPa; \( x \) is the far ultraviolet exposure, and ESH.

Fitting the elongation of film after 300ESH far-ultraviolet exposure shows that the elongation of the film increases exponentially with the far-ultraviolet exposure:

\[ y = 51.053 - 15.259 \exp \left( - \frac{x}{630.543} \right) \quad (x>300) \]

Here, \( y \) is the elongation, %; \( x \) is the exposure of far ultraviolet, ESH.

It can be seen that the tensile strength and elongation of the polyimide film decrease first and then increase exponentially with the far ultraviolet exposure.

4. Physical Models of Mechanical Properties of Polyimide

4.1. Microstructure Change
XPS analysis was performed on the C, N, and O of the PI film their percentages are shown in Table 1.
Table 1. Component percentage of PI in FUV irradiations

| irradiance/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 the Table 1, it can be seen that the percentage of C in PI by far UV irradiation decreases firstly and then increases, and the percentage of O and N increases firstly and then decreases, which indicates that under far UV irradiation, the fracture of the molecular valence of the PI film occurs firstly and results in the enrichment of N and O on the surface. After further irradiation, O and N become small molecules and are released, causing the increase of C and the cross-linking reaction appear. The performance of the PI film is decreased firstly and then increase. The molecular formula of polyimide is shown in Figure 3.

![Molecular structural formula of polyimide](image)

Figure 3. Molecular structural formula of polyimide

The chemical valence of C and its changes before and after the far ultraviolet irradiation were shown in Table 2.

Table 2. Functional group of PI before and after FUV irradiation

| peak/eV | 0 | 300ESH | 1000ESH |
|---------|---|--------|--------|
|         | Intensity/CPS | Percent/% | Intensity/CPS | Percent/% | Intensity/CPS | percent/% |
| 284.4   | — | —      | 11859.28 | 11.79  | 13329.2  | 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   | —       | —      | —        | —      |
| 284.4   | — | —      | 11859.28 | 11.79  | 13329.2  | 14.57  |

In Table 2, the peak position 284.4eV represents the substitution reaction between ring 2 and ring 3 to generate C (1,2,3,4,5,6), and the peak position 284.7eV represents the C (2,2,3 of ring 2 and ring 3), 3,5,6) and C (2,5) of ring 1, peak position 285.6eV represents C (1) of ring 2 and C (4) of ring 3, peak position 286.2eV represents C (4 of ring 2) ) And C (1) of ring 3, the peak position of 288.2 eV represents the C = O bond, and the peak position of 288.2 eV represents the CN bond. From the analysis in Table 3 and Figure 5, it can be seen that with the increase of far-ultraviolet radiation, the CO film of the PI film breaks first. At this time, the cross-linking has not yet occurred, and the fracture is mainly caused by the increase of C = O. It is shown that the increase of CON, while the COC continues to decrease. Therefore, the tensile strength decreases first and then increases. The percentage decrease of C = O is due to the breakage of COC and CN, the C (4) of ring 2 and the C (1) of ring 3 are cross-linked, so it appears as C (2,3,3 of ring 2 and ring 3) 5,6) CO (284.4) increased.

Further analysis of the chemical valence bond of element N was performed and the change of its functional groups was shown in Table 3.
In Table 3, the peak position of 531.8 eV represents a C = O bond, a peak position of 532.2 eV represents a -N (C (O)) bond, and a peak position of 533.1 eV represents a C-O-C bond. From the analysis in Table 3, it can be seen that in the early stage of far-UV irradiation, COC fracture occurred first, and at this time, cross-linking had not yet occurred. Fracture was the main cause. The percentage of C = O increased and the percentage of CO increased. The content decreased, followed by cross-linking, which showed an increase in CON, while COC continued to decrease. Therefore, the tensile strength decreases first and then increases. During the far ultraviolet irradiation, C = O did not break, but the C-O-C bond decreased until it disappeared. The complete fracture of C-O-C occurred when the exposure was 300ESH, which was related to the minimum tensile strength at this time.

Further analysis of the chemical valence bond of element N was performed and the change of its functional groups was shown in Table 4.

### Table 3. Functional group of O in polyimide before and after FUV irradiation

| peak/eV | 0ESH | 300ESH | 1000ESH |
|---------|------|--------|---------|
|         | intensity/CPS | percent/% | intensity/CPS | percent/% | intensity/CPS | percent/% |
| 531.8   | 38632.45 | 71.17  | 13514.58  | 21.06     | 23715.47 | 36.33     |
| 532.2   | —     | —      | 41509.86  | 64.69     | 19280.24 | 29.53     |
| 533.1   | 15647.97 | 28.83  | 9144.681  | 14.25     | 22289.69 | 34.14     |

In Table 3, the peak position of 531.8 eV represents a C = O bond, a peak position of 532.2 eV represents a -N (C (O)) bond, and a peak position of 533.1 eV represents a C-O-C bond. From the analysis in Table 3, it can be seen that in the early stage of far-UV irradiation, COC fracture occurred first, and at this time, cross-linking had not yet occurred. Fracture was the main cause. The percentage of C = O increased and the percentage of CO increased. The content decreased, followed by cross-linking, which showed an increase in CON, while COC continued to decrease. Therefore, the tensile strength decreases first and then increases. During the far ultraviolet irradiation, C = O did not break, but the C-O-C bond decreased until it disappeared. The complete fracture of C-O-C occurred when the exposure was 300ESH, which was related to the minimum tensile strength at this time.

Further analysis of the chemical valence bond of element N was performed and the change of its functional groups was shown in Table 4.

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

| peak/eV | 0 | 300ESH | 1000ESH |
|---------|---|--------|---------|
|         | intensity/CPS | percent/% | intensity/CPS | percent/% | intensity/CPS | percent/% |
| 399.81  | 2449.84 | 18.32  | 1392.982 | 10.09     | 2698.966 | 23.34     |
| 400.4   | 10924.78 | 81.68  | 8581.198 | 62.18     | 3913.804 | 33.84     |
| 400.8   | —     | —      | 3826.958 | 27.73     | 4952.307 | 42.82     |

In Table 4, the peak positions of 399.81 eV, 400.4 eV, and 400.8 eV represent the -N (C (O)) bond, the C-N bond, and the N element, respectively. It can be seen from Table 4 that the gradual increase of 399.8 eV and the decrease of 400.4 eV of the N element indicate that an increase in the fracture of C-N occurred. At the same time, the gradual increase of the peak position of 400.8 eV indicates the precipitation of N and enrichment on the surface.

### 4.2. Microstructure Evolution

The bond energy of the molecular bonds in the PI film such as C-C, C-H, C-N, C-O, C=O, Benzene ring is 3.47eV, 4.32 eV, 3.17 eV, 3.73 eV, 7.64 eV, 21.55 eV~29.78 eV separately. Since the spectral range of the deuterium lamp is 115nm ~ 200nm, the corresponding photon energy is 3.1eV ~ 6.2eV, which can destroy other valence bonds of PI except benzene ring.

Under the action of far-ultraviolet irradiation, the chemical valence of PI film react with high-energy ultraviolet photons and results in the break and crosslink of valence bond of PI film, which leads to the change of mechanical properties of PI film.

From Table 3, it can be analyzed that the C-O-C bond content is significantly reduced under far ultraviolet irradiation, which indicates that the fracture of C-O in PI film by far ultraviolet irradiation between ring 2 and ring 3 (corresponding 286.2 eV peaks) occurred. According to the change of the valence bond of the N element, it can be inferred that the C-N bond disappeared under the far-ultraviolet irradiation, which shows that the C-N bond between the PMDA molecular chain and the ODA molecular chain in Fig. 6 is basically absent under the action of the far-ultraviolet photon. According to the change of the molecular bond of C in the ODA molecular chain, it can be know that the ring 2 and the ring 3 develop toward the pure benzene ring due to the rupture of the C-N bond and the C-O bond. From the change of the C valence bond element, it can be seen that the PMDA molecule chain changes to the pure benzene ring firstly and then combines with the C = O bond and
part of the N ions, which leads to the percentages of 285.6eV and 288eV increased firstly and then decreased.

Therefore, in the initial stage of far-ultraviolet irradiation, C-O, C-C, C=O, C-H, and C-N equivalent bonds can be broken by the energy of far-ultraviolet photons, and the following molecular chain breaking reactions occur.

\[
\text{(1) } \quad \text{C-O, C-C, C=O, C-H, and C-N equivalent bonds can be broken by the energy of far-ultraviolet photons.}
\]

\[
\text{(2) } \quad \text{Further reactions occur with the breaking of these bonds.}
\]

\[
\text{(3) } \quad \text{These reactions lead to the formation of new bonds and ions.}
\]

\[
\text{(4) } \quad \text{The new bonds and ions formed in the previous steps further react to form more stable structures.}
\]

\[
\text{(5) } \quad \text{The final products of these reactions are stable compounds.}
\]

At the beginning of far-ultraviolet irradiation, the fracture reaction equation of PI film under the action of far-ultraviolet photons is:

\[
\text{(10) } \quad \text{Due to the little bond energy of the C-N bond, N element will exist as N ions under the action of far ultraviolet rays, and most of them will dissociate, and a minority of the N ions may undergo a recombination reaction with the C-O bond in an unstable ionic state as the following equation.}
\]
\[ \text{C}^4 + \text{O}^2 \rightarrow \text{C} - \text{O} \quad (11) \]
\[ \text{C}^4 + \text{N}^3 \rightarrow \text{C} - \text{N} \quad (12) \]
\[ \text{C} - \text{O} + \text{N}^3 \rightarrow \text{C} - \text{O} - \text{N} \quad (13) \]
\[ \text{C} - \text{O} \rightarrow \text{N}^3 \rightarrow \text{C} - \text{O} \quad (14) \]
\[ \text{C} - \text{O} \rightarrow \text{N} \rightarrow \text{C} - \text{O} \quad (15) \]
\[ \text{C} - \text{N} \rightarrow \text{C} + \text{O} \quad (16) \]

With the increase of far ultraviolet irradiation, the complete dissociation of N element will occur. It can be inferred that following cross-linking reactions may exist with the far ultraviolet radiation:

\[ \quad (17) \]
\[ \quad (18) \]
\[ \quad (19) \]

5. Conclusions
Following conclusions can be obtained:
(1) Under far-ultraviolet irradiation, the tensile strength and elongation of PI films decrease firstly and then increase exponentially until stabilize.
(2) In the initial stage of far-ultraviolet irradiation, the fracture of C = O bond, C-O bond, C-N bond, and C-C bond is the main reason for the degradation of its mechanical properties.
(3) With the increase of the far-ultraviolet exposure, N element will be precipitated from the PI film and enriched on the film surface. At the same time, some C = O bond and C-O bond will recovery too.
(4) Crosslink reactions will occur between C ions, N ions, and O ions with benzene rings or between different benzene rings. At the same time, C-O bonds and C-N bonds will gradually disappear.

6. Acknowledgments
This work supported by National Natural Science Foundation of China(No.11975052), Key Program for International Science and Technology Cooperation Projects of China(No.2018YFE0118000) and National key program(No.JSHS2016203A001).

7. References
[1] R. Verker, E. Grossman, N. Eliaz 2009 Acta Materialia 57 1112
[2] Hiroyuki Shimamura and Ichiro Yamagata 2009 Journal of spacecraft and rockets 46 15
[3] Joyce A D, Kim K G, Jacqueline A T 1998 AIAA 0895 1
[4] Stuckey W K, Meshishnek M J, Hanna W D, et al 1998 Aerospace Report TR-98(1055)-1 1
[5] Albarado T L, Hollerman W A, Edwards D 2005 *Journal Solar Energy Engineering* **127** 125
[6] Dennis A R, John W C, Lawrence B F, et al 2001 *AIAA* **1414** 1
[7] David E, Whitney H, Tesia S, et al 2002 *SPIE* **4823** 67
[8] David E, Charles S, Mary H, et al 2004 *SPIE* **5554** 80
[9] Shen Zicai, Zheng Huiqi, Zhao Xue, et al 2010 *Spacraft Environment Engineering* **27** 600
[10] Zhang Fan, Shen Zicai, Feng Weiquan, et al 2012 *Spacraft Environment Engineering* **29** 315
[11] Huang Xiaoqi, Wang Li, Liu Yufei, et al 2014 *Vacuum and Cryogenics* **20** 154
[12] Shen Zicai, Mu Yongqiang, Wu Yiyong 2015 *Equipment Environment Engineering* **12** 42