Carbon K-edge x-ray absorption spectroscopic analysis of photo-degraded polyimide film

Tomoaki TANAKA*[1, 2], Kyoko K. BANDO[1], Nobuyuki MATSUBAYASHI[1], Motoyasu IMAMURA[1], Hiromichi SHIMADA[1]
[1]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan
[2]New Energy and Industrial Technology Development Organization, Toshima-ku, Tokyo 170-6028, Japan

Introduction

The environmental modification of polyimide film is with considerable industrial interests. Pyromellitimido-oxydianiline (PMDA-ODA) polyimide (PI), known as Kapton films, have widely been used in many industries due to the excellent physical and thermal properties. One of the recent applications of the PMDA-ODA PI film has been found in the aerospace industry as thermal blankets. In this situation, the polyimide films are exposed to the aerospace environment and thus damaged by strong UV irradiation. The purpose of the present study is to elucidate the structural changes of PMDA-ODA PI films when exposed to the strong UV irradiation. For this purpose, we have prepared PMDA-ODA PI films exposed to an UV light source and analyzed the structural changes by using x-ray absorption spectroscopy (XAS).

Experimental

The carbon K-edge XAS measurements were performed at the BL-13C with the partial electron yield (PEY) method using a micro-channel-plate (MCP). Our XAS measurement system can overcome the problem of charging of sample surface using an electron flood gun that can supply a large current of low energy electrons to the sample surface [1]. The XAS spectrum was obtained by dividing the PEY signals by *Io* intensity that was separately acquired by measuring the total electron yield from a sputtered Au plate. This is quite important because the *Io* profile exhibited a large intensity modulation at the carbon K-edge region due to the carbon contamination on the beam line optics. The polyimide films analyzed were non-irradiated and UV irradiated PMDA-ODA PI films for 10, 30 and 60 minutes with a diameter of 5 mm and a thickness of 10 m. A low-pressure mercury lamp was used as the UV light source.

Results and discussion

Figure 1 indicates a unit structure of PMDA-ODA PI that consists of PMDA and ODA subunits. The carbon K-edge XAS spectra of the PMDA-ODA PI film are shown in figure 2. Each peak of the carbon K-edge XAS spectrum is interpreted as transitions from C1s to the π^*(C=C, C=O), σ^*(C-O, C-N, C=C) resonance for the PMDA and ODA subunits. The assignments of these transitions described in Table 1 were done based on a report [2] and shown in Fig. 2. All the σ^* and π^* features from the aromatic ring carbons of the PMDA and ODA unit decreased with increasing the UV irradiation time. These observations suggest that the UV irradiation broke some bonding and produced new bonding that resulted in the degradation of the ordered PMDA-ODA structure. The intensity of the π^* feature assigned to the transition to C=O in the imide group of PMDA unit most significantly decreased. It is very likely that the PMDA ring was selectively cleaved, whereas relatively small change took place in the ODA unit. At the same time, the intensity of a new peak at 288.1 eV increased with increasing the UV irradiation time.

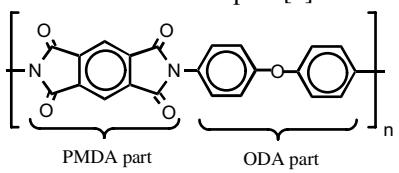

Figure 1 Unit structure of PMDA-ODA PI films

According to building block approach, this peak can be assigned to a carboxyl group. We find that the UV irradiation caused cleavage of imide rings of PMDA units that resulted in the formation of carboxyl groups. Further study is needed to conclude the structural changes caused by UV irradiation.

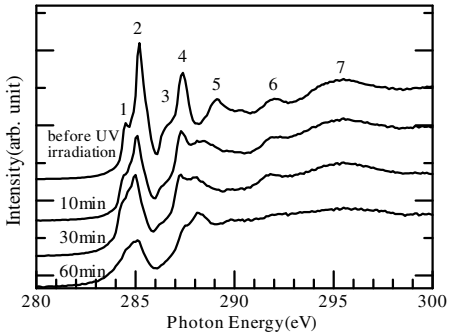

Figure 2 C K-edge XAS spectra of PMDA-ODA PI film; before UV irradiation, UV irradiation of 10, 30 and 60min

Table 1 Assignments and positions of polyimide film of PMDA-ODA type

	Peak (eV)	Ref.[2]	Assignment
1	284.5	284.8	π^*(C=C) (PMDA)
2	285.2	285.2	π^*(C=C) (ODA)
3	286.41	286.6	π^*(C=C) (ODA)
4	285.7	287.4	π^*(C=O)
5	289.4	289.2	π^*(C=C) (PMDA, ODA)
6	292.2	291.9	σ^*(C-O, C-N)
7	295.6	295.4	σ^*(C=C) (ODA)

References

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* tanaka-t@aist.go.jp