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A characterization of Kapton polyimide by X-ray photoelectron spectroscopy and energy dispersive spectroscopy

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Kapton polyimide films were characterized by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS). The samples characterized include Kapton-H and Kapton-HN. The XPS data suggest that the Kapton films are mainly poly(4,4′-oxydiphenylene pyromellitimide). The Kapton-HN films were found to have imbedded particles which were identified by EDS to contain calcium and phosphorus. These films also give solid residues of approximately 0.4 wt% after the films were heated to 800° C in air.

1. Introduction

There is much interest in using polyimides for various applications because of their unique chemical and physical properties. These materials are particularly useful in high temperature applications and have been used at temperatures up to 400° C. In some industries where there may be extreme demands on the quality of products fabricated from polyimide films, a thorough understanding of the material ingredients and properties is critical. Unfortunately, such information is sometimes not available from manufacturers of polyimide films. In this paper, we present the results of XPS and EDS studies of two polyimides tradenamed Kapton-H and Kapton-HN.

2. Experimental details

Kapton-H and Kapton-HN films were purchased from E. I. DuPont de Nemours and Company. They were 50 μm in thickness. The XPS data were obtained with an extensively modified AEI ES-100 photoelectron spectrometer. Modifications to this instrument include the addition of a 200 l sec^{-1} turbomolecular pump and a 110 l sec^{-1} ion pump for evacuation of the sample chamber. Data collection on the XPS instrument was accomplished with a Motorola 68000-based microprocessor which was interfaced to a VAX 11/780 minicomputer. All data processing was accomplished with custom software developed on the VAX computer. SEM photomicrographs were obtained with a JEOL 840 instrument equipped with an Ortec energy dispersive spectrometer (EDS).

3. Results and discussion

The overall XPS spectrum of a Kapton-HN sample is shown in Fig. 1. Carbon, oxygen, and nitrogen signals can be clearly observed from this sample. A slight silicon surface contamination was also detected on two of three Kapton-HN samples that were analysed. The high resolution carbon 1s, oxygen 1s, nitrogen 1s, and silicon 2p signals are also reproduced in Fig 2 to 5, respectively. From Fig. 2, two main carbon peaks were observed at 289.0 eV and 285.7 eV binding energy with an intensity ratio of 1 to 4.5. The 289.0 eV signal is due to the carbon from C=O groups and the 285.7 eV signal from aromatic rings. About 6 to 7 eV higher in binding energy from the 285.7 peak, a weak signal was detected. This is identified to be a "shakeup" satellite of the aromatic groups due to $\pi \rightarrow \pi^*$ transitions [1, 2].

The oxygen 1s, nitrogen 1s and silicon 2p peaks were detected at 532.1 eV, 400.1 eV, and 101.2 eV binding energies respectively. The XPS data are tabulated in Table I. Each of the values given in this table is the mean and standard deviation of measurements on three different samples. The atomic percent compositions were obtained by dividing the signal

TABLE I Theoretical and measured XPS data of Kapton-HN and Kapton-H (poly(4,4′-oxydiphenylene pyromellitimide))

XPS Signal	Carbon 1s		Oxygen 1s	Nitrogen 1s	Silicon 2p
Binding energy (eV)	289.0	285.7	532.1	400.1	101.2
Theoretical atomic %	13.8	62.1	17.2	6.9	–
Measured atomic % (Kapton-HN)	13.5 ± 1.9	60.0 ± 1.8	18.2 ± 0.7	7.1 ± 0.2	1.0 ± 1.0
Measured atomic % (Kapton-H)	14.7 ± 0.9	59.9 ± 0.8	17.6 ± 0.3	7.5 ± 0.2	–

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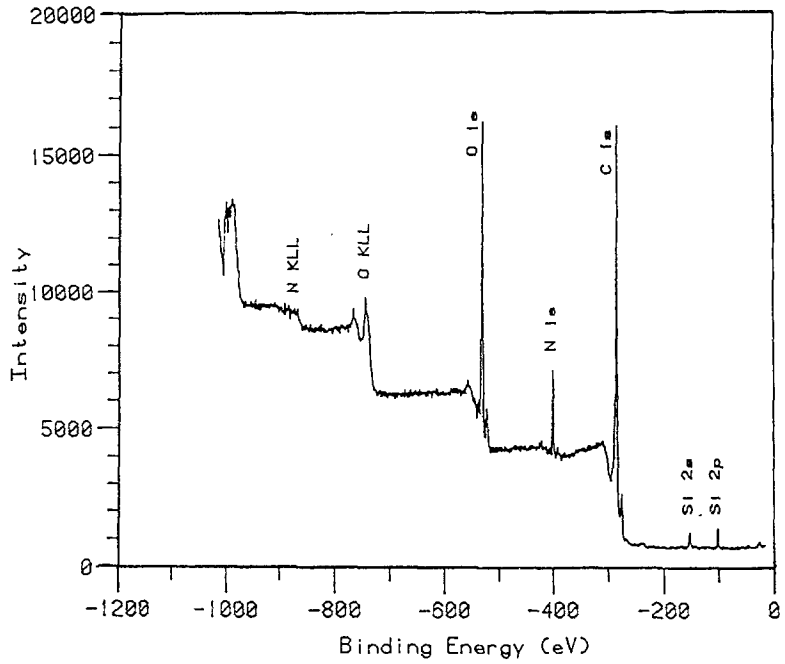

Figure 1 Overall XPS scan of a Kapton-HN sample.

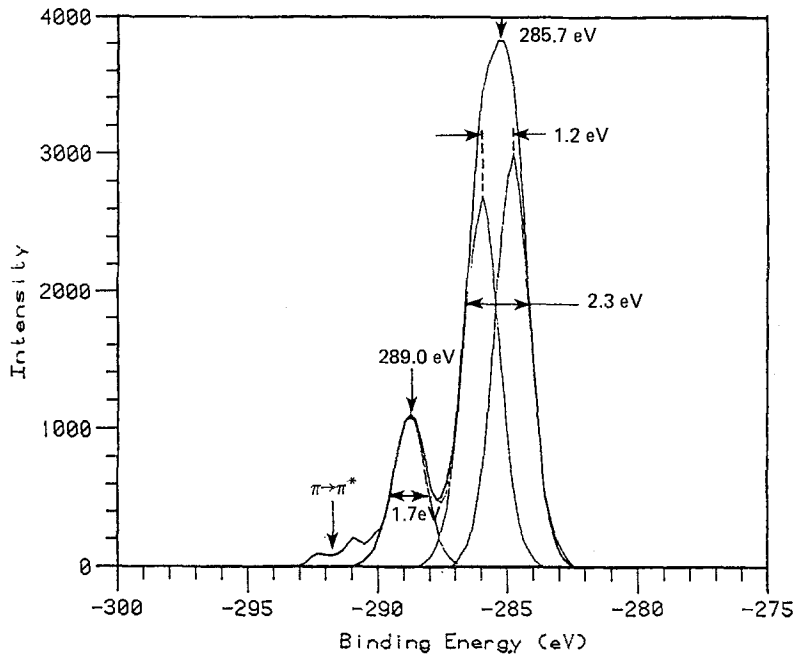

Figure 2 High resolution carbon 1s XPS spectrum of a Kapton-HN sample.

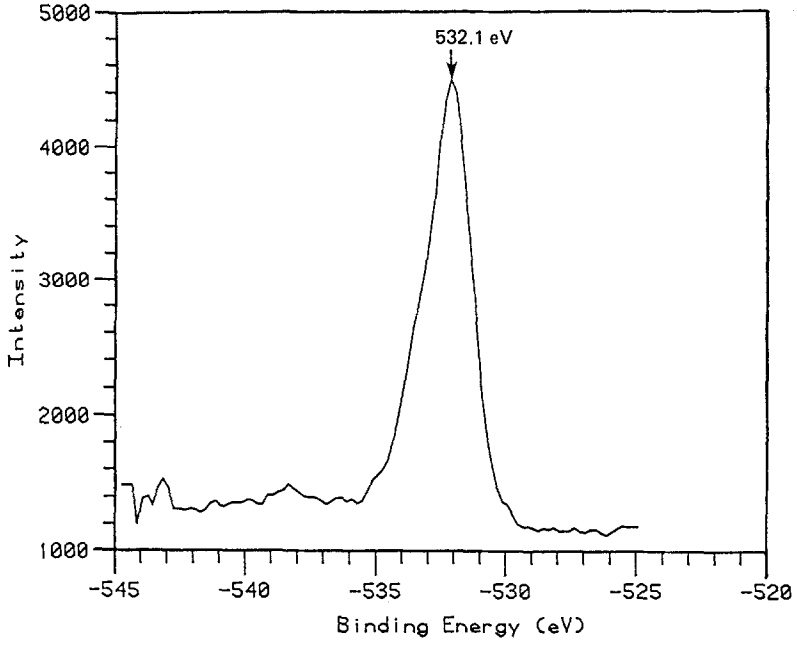

Figure 3 High resolution oxygen 1s XPS spectrum of a Kapton-HN sample.

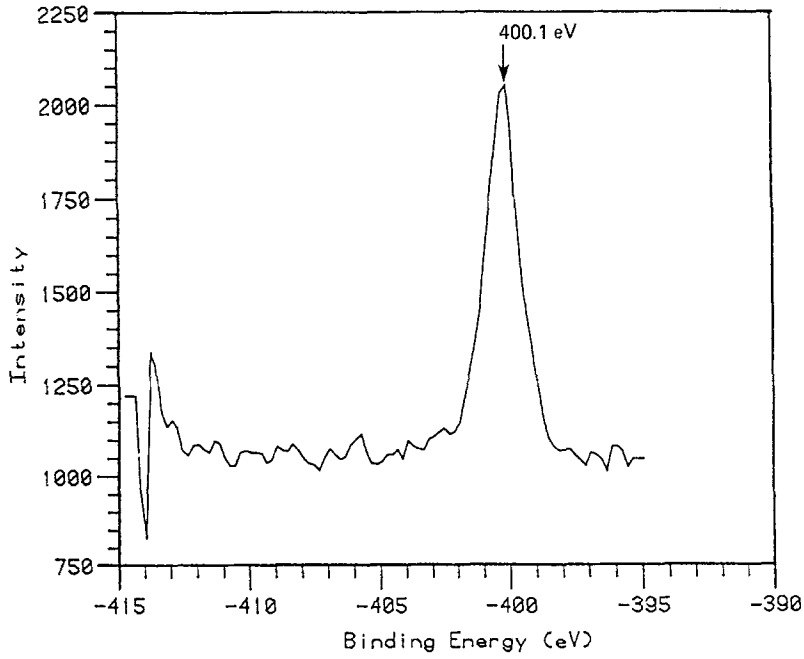

Figure 4 High resolution nitrogen 1s XPS spectrum of a Kapton-HN sample.

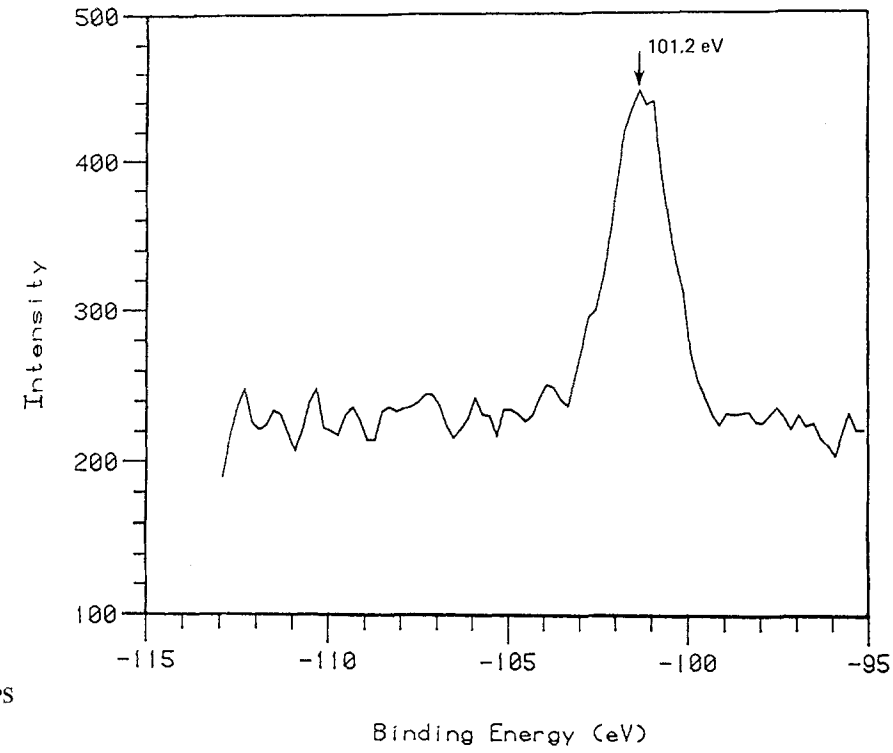

Figure 5 High resolution silicon 2p XPS spectrum of a Kapton-HN sample.

intensities by cross-section factors (0.25 for carbon 1s, 0.60 for oxygen 1s, 0.40 for nitrogen 1s, and 0.28 for silicon 2p) [3]. Note that the atomic ratio of nitrogen to oxygen is very close to 2 : 5 for all six runs we made. This strongly suggests that the main ingredient of Kapton is a poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-ODA). A monomeric structure is reproduced in Fig. 6, and the theoretically predicted XPS data were calculated and are shown in Table I. Our experimental results agree extremely well with those calculated.

From the carbon 1s data in Fig. 2, the atomic ratio of carbonyl group (289.0 eV) to the benzene group (285.7 eV) is indeed 4 to 18. However, an obvious line broadening can be observed in the 285.7 eV peak (2.3 eV wide at half intensity). This means that among the 18 carbons, there are at least two different groups [4–6]. We suggest that the 18 carbons be subdivided into groups of 8 and 10 with peaks about 1.2 eV apart. Ten are from the carbons bonded to hydrogens (two from pyromellitic dianhydride (PMDA) and eight from oxydianaline (ODA)). The remaining eight are from carbons bonded to oxygen, nitrogen, or carbonyl carbons.

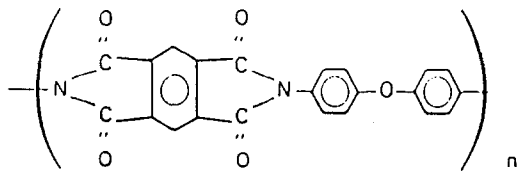

Figure 6 Monomeric structure of poly(4,4′-oxydiphenylene pyromellitimide).

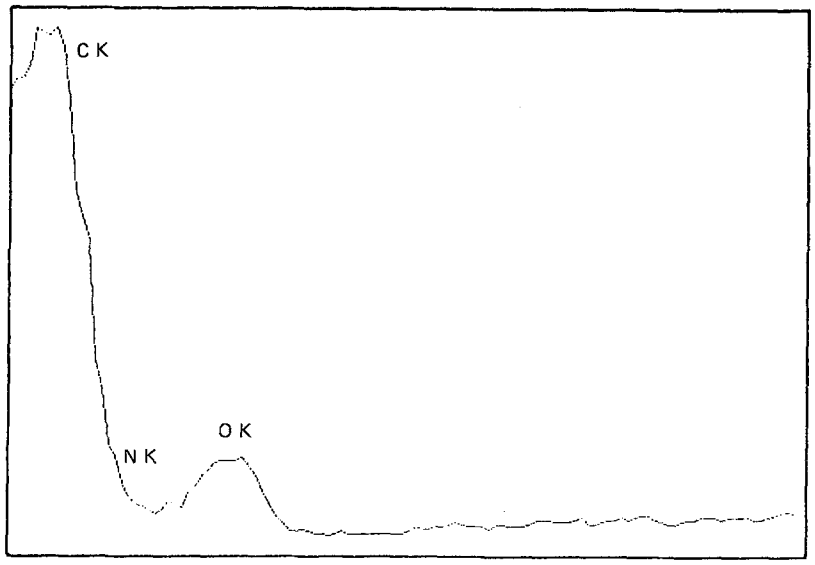

Figure 7 EDS spectrum of a Kapton-HN sample.

Careful attention should also be paid to the lineshape of the oxygen 1s peak which shows a certain degree of asymmetry. The oxygen 1s lineshape shown in Fig. 3 is identical to that which has been reported for PMDA-ODA [6]. There are four oxygens from the PMDA and one from the ODA. The ODA oxygen 1s peak is seen as a shoulder on the higher binding energy side of the main oxygen 1s peak.

Energy dispersive spectroscopy (EDS) was also used to characterize these polymeric films. A typical EDS spectrum is shown in Fig. 7 which clearly indicates carbon, nitrogen, and oxygen. Investigation of Kapton-HN films by optical microscopy shows numerous particles imbedded in the samples. Fig. 8 is an example of such a picture at 70 × magnification. No such particles can be found in the Kapton-H samples. Fig. 9 shows a particle in the Kapton-HN at 3500 × magnification under scanning electron microscopy (SEM). This photomicrograph was taken of the Kapton-HN sample in cross section. The particle which can be seen in this photo is about 5–6 μm in diameter and is one of the largest particles present in this sample. EDS shows calcium and phosphorus signals at this spot. No such signals were detected from the regions away from this spot (Fig. 10). Apparently these particles are additives to Kapton-HN. None of these additives were detected in the Kapton-H films.

When the Kapton-HN films were ashed in air at 800° C, approximately 0.4 wt % of white solid residue was left. There was no residue from the H samples after ashing in air. These white solids were also found to contain calcium and phosphorus. The EDS spectrum is shown in Fig. 11. Comparing Figs 10 and 11, it is obvious that the calcium to phosphorus ratio is smaller in Fig. 10. This is probably due to the difference in the sample geometry.

4. Conclusions

The XPS data indicates that Kapton-H and Kapton-HN are both PMDA-ODA polyimides. Optical microscopy and SEM studies showed that Kapton-HN contained well dispersed fine particulates. EDS analysis showed that these particles contained calcium and phosphorus, and are probably calcium phosphate. When a Kapton-HN sample was ashed in air, 0.4 wt % of the calcium phosphate residue remained. No particulate was observed in the Kapton-H sample, and there was no residue after the sample was ashed.

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Figure 8 Optical micrograph at 70 × of a Kapton-HN sample.

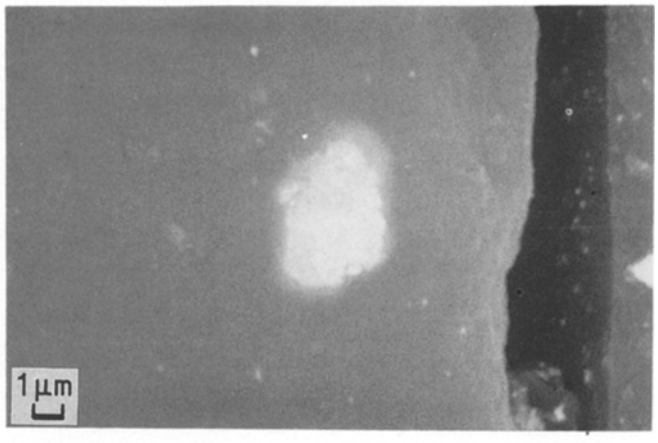

Figure 9 SEM cross-section picture at 3500 × of a spot from a Kapton-HN sample.

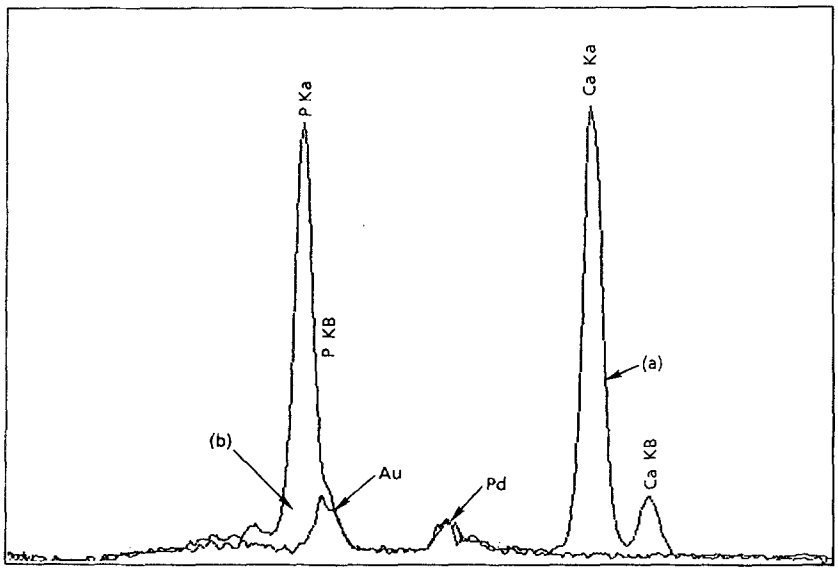

Figure 10 EDS spectra of a Kapton-HN sample: (a) at spot; (b) off spot.

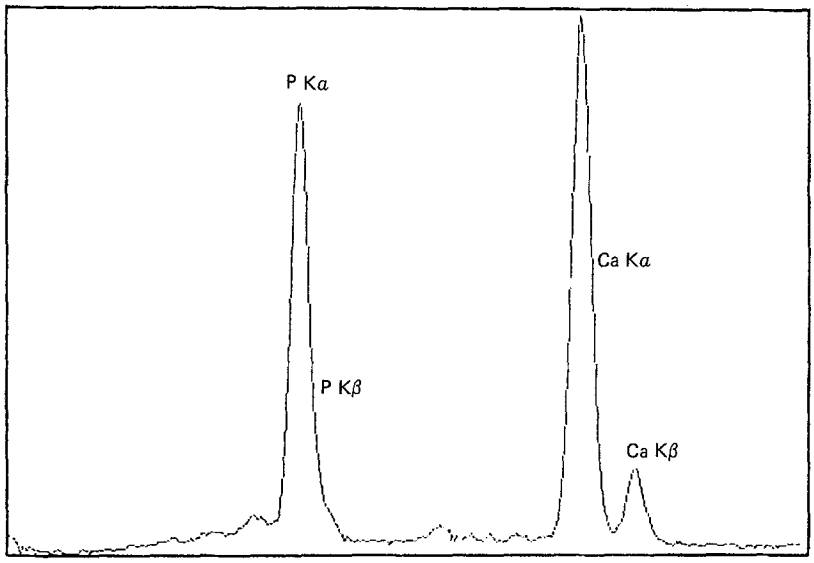

Figure 11 EDS spectrum of solid residues from a Kapton-HN film ashed at 800° C in air.

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