Properties and structure of vapor-deposited polyimide upon electron-beam irradiation

F.-Y. Tsai[a] and Y.-H. Kuo
Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

D. R. Harding
Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623

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Vapor-deposited polyimide capsules from pyromellitic dianhydride and 4,4′-oxydianiline were irradiated with an electron beam that mimicked the β-radiation emitted by tritium, a fuel that the capsules are to contain during the inertial confinement fusion process. The mechanical properties and gas permeability of the irradiated capsules were measured to examine their radiation resistance. Upon electron-beam irradiation at an energy of 8 keV and a dose of 120 MGy, the capsules showed 15% and 56% decrease in tensile strength and elongation at break, respectively, without significant change in gas permeability and Young's modulus. Analyses using x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy indicated that the chain cleavage and carbonization occurred but were confined in a thin layer at the top surface of the capsules. The shallow penetration of the low-energy electron beam used, as well as the existence of cross-linking in the vapor-deposited polyimide, may have led to the smaller magnitude of property degradation in the capsules compared to that reported for solution-cast polyimide. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2186030]

I. INTRODUCTION

Aromatic polyimides, with their excellent mechanical properties and thermal stability, have been proposed as a promising material for the inertial confinement fusion (ICF) target, a millimeter-sized spherical capsule holding hydrogen isotopes to be placed at the focal point of fusion-triggering laser beams.[1,2] Previous efforts have made possible the fabrication of aromatic polyimide capsules from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) by employing a technique based upon vapor-phase polymerization,[3–5] or by an emulsion technique,[6] and the properties of the capsules critical to the ICF application were assessed.[7–10] It was verified that the PMDA-ODA polyimide capsules, prepared via the vapor-deposition technique, possessed comparable yet distinct properties from the commercial PMDA-ODA polyimide (Kapton), produced by solution-based methods. Prior works have yet to examine one attribute of the capsules vital to the ICF application: their resistance to β radiation emitted by tritium, a main component of the fuel mixture currently used in ICF. A polyimide capsule may absorb 60–120 M Gy of β radiation from tritium while being prepared as an ICF target,[11] which may significantly impact its performance. It is therefore important to determine the effects of β radiation on the polyimide capsules' ICF-related properties, i.e., gas permeability and mechanical properties.

Effects of electron-beam radiation on the mechanical properties of commercially available aromatic polyimides such as Kapton have been studied.[12] It was reported that upon irradiation by an electron beam (energy=2 MeV) to a dose of 120 M Gy, Kapton exhibited ~8% increase in Young's modulus, ~30% decrease in tensile strength, and ~80% decrease in elongation at break. Gas permeability of electron-beam-irradiated PMDA-ODA polyimide has not been studied; however, Kita *et al.* reported reduced gas permeability through benzophenone-containing polyimide that was irradiated with an electron beam, and attributed the decrease in permeability to radiation-induced cross-linking.[13] As to the structural changes brought about by β radiation, Tahara *et al.* conducted x-ray photoelectron spectroscopy (XPS) on E-beam (20–30 keV) irradiated PMDA-ODA polyimide to observe rupture of the imide linkage.[14]

β radiation emitted by tritium is of lower energy than that of the E-beams used in previous study; i.e., its energy is distributed between 0 and 16 keV, averaging at 8 keV. This study sought to examine the properties of vapor-deposited polyimide capsules irradiated with an E-beam mimicking β radiation emitted by tritium, in the meantime investigating some of the previously unexplored topics: (1) β-radiation resistance of vapor-deposited polyimide, (2) effects of low-energy E-beam radiation on the properties of polyimide upon extended exposure, and (3) gas permeability of E-beam-irradiated PMDA-ODA polyimide. XPS and infrared absorption spectroscopy analyses were carried out on irradiated samples to determine the induced structural changes.

II. EXPERIMENT

A. Sample preparation

Polyimide capsules were prepared via a vapor-deposition technique, which involved two steps: (1) the monomers, PMDA and ODA, were coevaporated in high vacuum onto spherical capsules made of poly-α-methylstyrene (PAMS) to

[a]Electronic mail: ftsai@ntu.edu.tw

form a layer of poly(amic acid), (2) the coated poly(amic acid) was converted into polyimide by thermal curing, where the PAMS capsules depolymerized into gaseous products that escaped by permeation, leaving behind the freestanding polyimide capsules. Detailed descriptions of the sample preparation process were reported previously.[15] PMDA and ODA were purchased from Sigma-Aldrich and used as received. PAMS capsules were purchased from General Atomics and used as received. The dimensions of the capsules were: outer diameter=950–1200 μm; wall thickness =3–7 μm. The capsules were screened for a minimum sphericity of 99.8% before testing.

B. Electron-beam irradiation

Polyimide capsules were irradiated with an electron beam in a Leica Cambridge S360 scanning electron microscope (SEM). The capsules were contained in a piezoelectric holder, which constantly agitated the capsules to achieve uniform irradiation. The electron beam was defocused to cover the whole area of the capsule holder (1 cm in diameter). The energy of the electron beam was 8 keV. The capsule holder was wired to an ammeter to monitor the incoming electron current, with which the total irradiation dose absorbed by the capsules was calculated. The electron current density was 7 mA/cm^2. With the assumption that electrons impinging on a capsule are completely absorbed, which is generally the case for polymeric materials, the absorbed radiation dose (in gray) was calculated by multiplying the electron current density with cross-sectional area of the capsule and the total irradiation time. The doses of E-beam radiation were selected to match the doses absorbed by a polyimide capsule during ICF target preparation, i.e., 60–120 M Gy.

C. Measurement of properties

The Young's modulus of the polyimide capsules was determined in a buckle test, where the maximum pressure differential a capsule could withstand before buckling was measured, which is known to be proportional to the Young's modulus. The tensile strength and elongation at break were determined in a burst test, where the maximum pressure differential (proportional to tensile strength) and maximum inflation (proportional to elongation at break) that a capsule could withstand before bursting were measured. Measurement of the gas permeability involved: (1) fill a capsule with a gas by permeation to a desired pressure; (2) transport the filled capsule to an evacuated chamber; (3) monitor the rate of pressurization in the chamber; and (4) calculate the permeability value from the measured pressurization rate. All measurements were done at room temperatures. For the detailed descriptions of the buckle test, burst test, and permeability measurement, the readers are referred to the previous publication.[15]

D. Surface analysis

Polyimide samples before and after irradiation were analyzed by the Fourier transform infrared spectroscopy (FTIR) (Bio-Rad FTS-3500) and XPS (VG Scientific Theta-Probe). FTIR spectra were taken in the transmission mode and the attenuated total reflection (ATR) mode. In the ATR measurements, a germanium prism was used, and the incident angle of the beam was set to 45°, resulting in a probing depth of 0.35 μm.[16] In the XPS measurements, monochromatized Al $K\alpha$ (1486.6 eV) x-ray was used, and charging effects were minimized by using an electron flood gun.

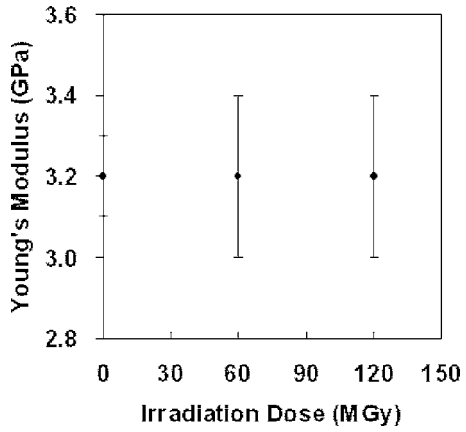

FIG. 1. Young's modulus of polyimide capsules as a function of E-beam irradiation dose.

III. RESULTS AND DISCUSSIONS

Mechanical properties of the polyimide capsules irradiated with 0, 60, and 120 M Gy are shown in Fig. 1 through Fig. 3. Gas permeability as a function of E-beam radiation dose is shown in Fig. 4. It can be seen from Figs. 1–4 that the Young's modulus and gas permeability did not change significantly upon 120 M Gy of radiation, while the tensile strength and the elongation at break were reduced by 15% and 56%, respectively. The degradations in tensile strength and elongation at break were much smaller than those reported for solution-cast commercial Kapton under the same radiation dose (30% and 80%, respectively, as described in the Introduction section). This difference may be attributed to the lower radiation energy used in this study, which effected the shallower penetration of the energetic electrons and thus more contained damage. The difference may also be due in part to the observation that vapor-deposited polyimide possesses certain degree of cross-linking, while solution-cast

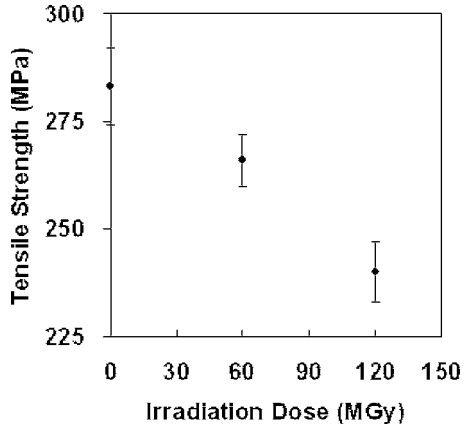

FIG. 2. Tensile strength of polyimide capsules as a function of E-beam irradiation dose.

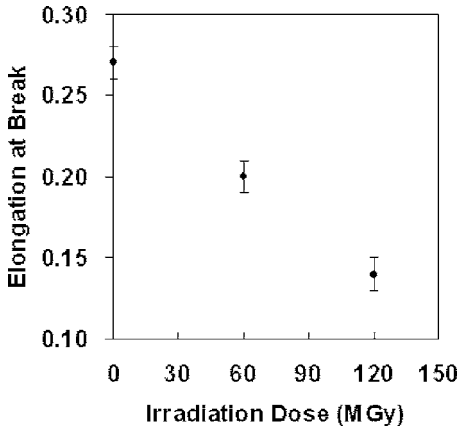

FIG. 3. Elongation at break of polyimide capsules as a function of E-beam irradiation dose.

polyimide is not cross-linked.[15] Cross-linking in a polymer increases its resistance to radiation-induced chain cleavage, thereby reducing the extent to which its tensile strength and elongation at break deteriorate.

FTIR spectra taken in the transmission mode, as shown in Fig. 5, show no discernable difference between the unirradiated and the irradiated (dose=120 M Gy) samples. In the ATR mode, on the other hand, the two samples gave rise to distinctively different spectra. The spectra of the unirradiated sample are identical in the transmission and ATR mode; however, the ATR spectrum of the irradiated sample show greatly diminished intensity at the polyimide characteristic peaks (1790, 1720, 1380 cm^{-1}, etc.) and a broad absorption band at 500–1000 cm^{-1}. These two features in the ATR spectrum suggest that the irradiated sample decomposed and experienced carbonization to a certain extent. The observation that the irradiated sample showed the altered FTIR spectrum only in the ATR mode but not in the transmission mode indicates that the radiation penetrated, and caused spectroscopically detectable changes in, only a small portion of the overall thickness of the sample. The 0.35 μm probing depth of FTIR employed in this study indicated that the radiation-induced changes were prominent in at least the 0.35-μm-thick layer at the top surface of the samples.

Figure 6 shows XPS C1*s* spectra of the unirradiated and

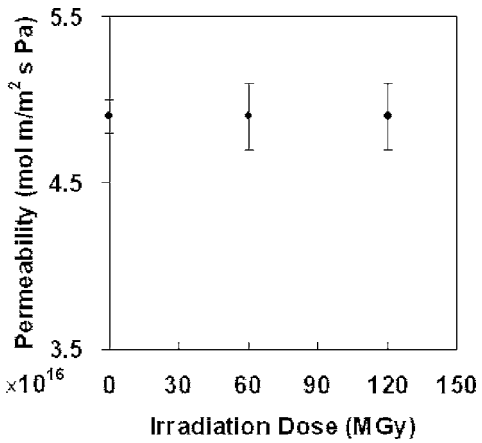

FIG. 4. Helium gas permeability of polyimide capsules as a function of E-beam irradiation dose.

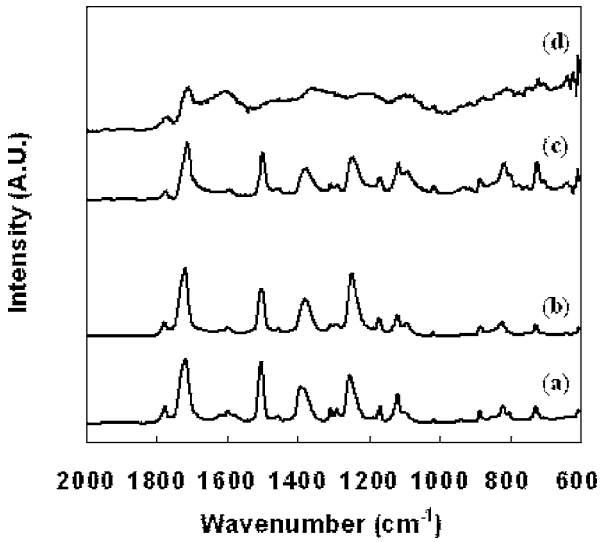

FIG. 5. FTIR spectra of unirradiated and irradiated (120 M Gy) polyimide samples: (a) unirradiated, transmission mode; (b) irradiated, transmission mode; (c) unirradiated, ATR mode; and (d) irradiated, ATR mode.

irradiated (dose=120 M Gy) samples, taken at the top surface; the atomic percentages of the fitting components are listed in Table I. The atomic percentages of C1*s*, N1*s*, O1*s*, and Si2*p* integrated from the XPS spectra are summarized in Table II. The silicon content came from contamination in the irradiation apparatus and the XPS system. Consistent with the FTIR observations, the irradiated sample showed reduced intensity in the imide linkage (CON), indicative of decom-

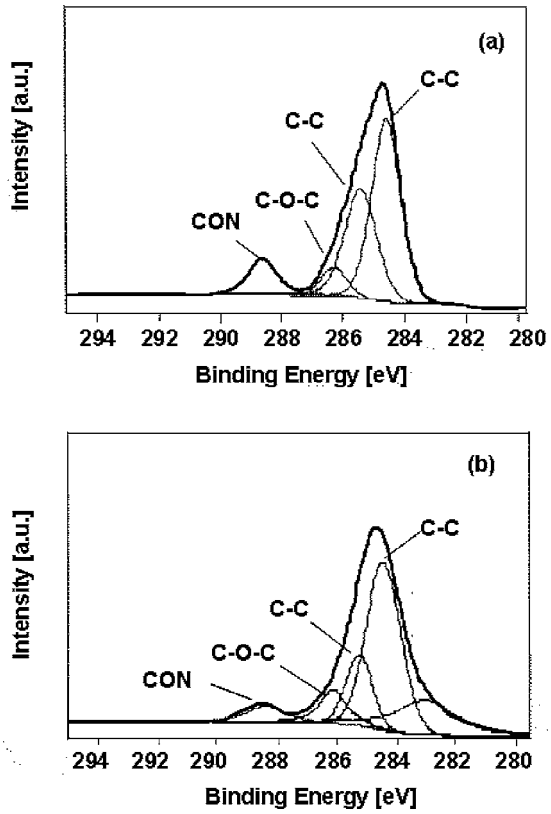

FIG. 6. XPS C1s spectra of (a) unirradiated, (b) irradiated (120 M Gy), samples. Note that C_1 corresponds to C–C sp^2 bonds and C_2 corresponds to C═O and C–N bonds.

TABLE I. XPS C1*s* fitting components for pristine (unirradiated) and irradiated samples (120 M Gy), where C_1 corresponds to C–C sp^2 bonds and C_2 corresponds to C=O and C–N bonds.

		At. %	
Peak	Centre B.E.	Unirradiated	Irradiated
a-C–Si	283.2	0	14.6
C_1	284.6	36.7	36.6
C_2	285.4	23.3	12.0
C–O–C	286.3	5.0	6.5
CON	288.5	7.4	4.4

position, and an additional peak at 283.2 eV that is attributable to amorphous carbon bonded with silicon (from contamination),[17] indicative of carbonization. These changes are reflected in the atomic contents where C had increased percentage while N and O contents decreased. The C–C sp^2 bonding (labeled as C_1) on the phenyl rings did not show an observable change, suggesting that the phenyl rings were largely intact. The increase in C–O–C content may be attributed to oxidation followed by the rupture of the imide linkage.

The FTIR and XPS analyses provide further insight on the mechanism of property changes in the polyimide capsules caused by E-beam irradiation. The properties that degraded detectably, tensile strength and elongation at break, are those associated with failure of a sample, while the unaffected gas permeability and Young's modulus are otherwise. The E-beam-inflicted damage was shown by FTIR to be confined in a thin layer near the top surface of the samples. The damaged top layer became brittle, enabling crack initiation at lower strain (elongation) and stress than does a pristine sample. Once initiated, the cracks in the top layer propagated through the bulk of the sample without sustaining much further strain and stress, thereby lowering the tensile strength and elongation at break. The Young's modulus and gas permeability, on the other hand, were still determined by the bulk material and therefore were largely unaffected.

TABLE II. Integrated percentages of C1*s*, O1*s*, N1*s*, and Si2*p* for pristine (unirradiated) and irradiated samples (120 M Gy).

	At. %	
Bonding	Unirradiated	Irradiated
C1*s*	72.5	74.0
N1*s*	4.9	3.9
O1*s*	17.2	16.9
Si2*p*	5.5	5.2

IV. CONCLUSION

Upon being irradiated with an electron beam of 8 keV energy to a dose of 120 M Gy, vapor-deposited polyimide capsules showed the unaffected Young's modulus and gas permeability, and 15% and 56% reduction in the tensile strength and elongation at break, respectively. FTIR in the transmission mode and ATR mode indicated that the E-beam-inflicted damage was confined to a thin layer at the surface of the samples, which underwent chain cleavage and carbonization. This observation was consistent with the XPS results. The smaller magnitude of property degradation of the vapor-deposited polyimide compared to that reported for solution-cast polyimide may be attributed to (1) cross-linking in the vapor-deposited polyimide, and (2) the lower E-beam energy used in this study, which effected the shallower penetration through the samples and thus more confined damage. The findings of this study will be useful in the design and handling of polyimide targets for the inertial confinement fusion experiments.

ACKNOWLEDGMENTS

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