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Low temperature fast-neutron and gamma irradiation of Kapton® polyimide films

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Abstract

Structure, chemistry and mechanical properties of Kapton® HA and H polyimide films have been studied after their exposure to fast-neutron and gamma irradiation at a target temperature of 4 K. The fast ($E > 0.1$ MeV) neutron fluence was 3.1×10^{22} n/m^2. X-ray diffraction showed that irradiation disordered partially crystalline structure of Kapton® H while the structure of Kapton® HA remained amorphous under irradiation. The glass transition temperature (T_g) of Kapton® HA and H increased with irradiation, consistent with the crosslink formation. The increase in T_g was significantly larger in Kapton® H. The FT-IR spectrometry showed no new absorptions in the irradiated Kapton® HA and H. Shifts in some peak positions have been observed, however. Tensile testing showed that irradiation increased modulus and yield strength of Kapton® HA and H, in agreement with the proposed crosslink formation as the predominant mechanism of radiation hardening. The extent of radiation hardening, as evaluated from the total strain at fracture, was significantly larger in Kapton® H.

1. Introduction

The magnets used to confine plasma in the international thermonuclear experimental reactor (ITER) will be subjected to unique operating conditions [1]. They will be operated at a target temperature of 4 K and will be exposed to high fast-neutron and gamma irradiation fluences and combined shear/compressive forces and fatigue. No repairs or replacements of magnets are anticipated over the 25-year lifetime. The current ITER insulation specifications for the toroidal field (TF) coil are as follows: 1×10^{22} n/m^2 fast-neutron fluence, 3×10^3 compression cycles, 20 cool-down cycles, 1 kV/mm operating voltage, 300 MPa compressive stress and 30 MPa shear stress.

Of the superconducting magnet components (i.e., superconductor, copper and insulation), the magnet performance will be most impaired by the sensitivity of the insulation to irradiation. Degradation of the mechanical strength of insulators at 4.2 K following fast-neutron and gamma irradiation is of particular concern. The candidate insulator materials for the ITER toroidal field coil insulation include vacuum pressure impregnation (VPI) and prepreg insulation systems, hybrid insulation systems, and fully inorganic insulation systems.

The hybrid insulation systems consist of a barrier or coating in combination with the VPI and prepreg primary insulation. Polyimide films and mica tape or sheet have been selected as candidate barrier materials. The candidate coating materials are plasma sprayed ceramics and polyimide coatings. Hybrid insulation systems are under consideration due to reliability concerns, namely, to improve electrical properties and irradiation resistance of the primary insulation [2].

In the research leading to this paper, structure, chemistry and mechanical properties of the Kapton® polyimide films have been studied after their exposure to low temperature fast-neutron and gamma irradiation. The pre-irradiated structure of Kapton® polyimide films was either fully amorphous (Kapton® HA, as designated by DuPont) or partially crystalline (Kapton® H, as designated by DuPont). The aim of this study was to provide an insight into the irradiation-induced changes in the properties of Kapton® polyimide films, relevant to their use as barrier materials in the ITER toroidal field coil insulation. The effects of 4 K fast-neutron and gamma irradiation on electrical strength

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constant (KV $mm^{-0.5}$) of Kapton® polyimide films have been reported elsewhere [3]. While the electrical strength constant of the unirradiated Kapton® HA exceeds that of Kapton® H, there was no significant difference in the measured postirradiation electrical strength constant of the two grades.

2. Experimental procedures

The unirradiated and irradiated Kapton® polyimide films were examined by using the following experimental techniques: X-ray diffraction, dynamic viscoelasticity, Fourier-transform infrared (FT-IR) spectrometry and tensile testing.

2.1. Neutron irradiation

Kapton® HA and H polyimide films were irradiated by using the low temperature irradiation facility TTB at the Munich Research Reactor. The in-core position is characterized by a thermal and fast ($E > 0.1$ MeV) neutron flux of $\Phi_{th} = \Phi_f = 3.1 \times 10^{13}$ cm^{-2} s^{-1}. The fast-neutron fluence was 3.1×10^{22} n/m^2. The gamma dose and the total dose were 3.6×10^7 and 6.7×10^7 Gy, respectively. The irradiation temperature was 4.2 K. Kapton® films subjected to irradiation had the following dimensions: 12.5 mm dia × 0.025 mm thick.

2.2. X-ray diffraction

X-ray diffraction spectra of the unirradiated and irradiated Kapton® HA and H polyimide films were obtained on Rigaku RU300 rotating anode generator and diffractometer. A copper anode was used and it was operated at 60 kV and 300 mA. Scan range was 3 to 100° and scan speed was 2°/min (2θ).

2.3. Dynamic viscoelasticity

The dynamic viscoelasticity of Kapton® polyimide films was measured as a function of temperature and frequency by using the DMS200 tension modulus (Seiko Instruments). This experiment enabled determination of the glass transition temperature (T_g) and its dependence on the neutron fluence. Specimen dimensions for the dynamic viscoelasticity measurements were typically 12 × 2 × 0.025 mm.

2.4. FT-IR spectrometry

Infrared spectrometry of Kapton® polyimide films was performed at the Bio-Rad, Digilab, Cambridge, MA. A research FT-IR microscope (model UMA 500) was used for this study. Specimen thickness was reduced from 25 μm to approximately 10 μm by using ion milling. The FT-IR microscope was operated in the transmission mode. In order to resolve some of the absorption bands, spectra were also acquired in the ATR (attenuated total reflection) mode.

2.5. Tensile testing

The unirradiated and irradiated Kapton® polyimide films (12.5 mm dia × 0.025 mm thick) were cut into 1 mm wide and 12 mm long strips. These sub-size specimens were tested in tension at room temperature by using an Instron machine and specially designed grips. Separation between the grips (which is equivalent to the specimen gauge length) was 6 mm. The crosshead speed was 12.7 mm/min. Due to a limited amount of the irradiated material available, three to four specimens have been tested for each condition.

3. Experimental results and discussion

3.1. X-ray diffraction

The structure of the unirradiated and irradiated Kapton® HA is shown in Fig. 1a and b, respectively. X-ray diffraction patterns of both the unirradiated and irradiated Kapton® HA show a broad peak in the range of 10 to 30° (2θ). This is a characteristic feature of all amorphous materials. It appears therefore that the structure of Kapton® HA, as formed during the process of thermal conversion, remained amorphous during the 4 K fast-neutron and gamma irradiation.

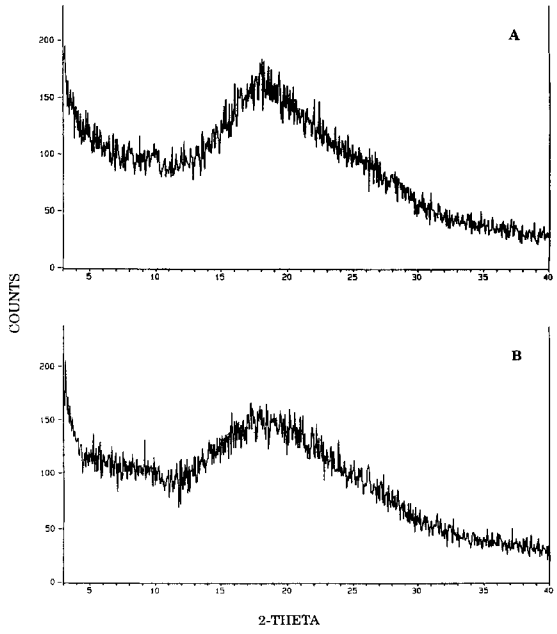

Fig. 1. X-ray diffraction pattern of Kapton® HA polyimide film: (A) unirradiated and (B) irradiated to 3.1×10^{22} n/m^2.

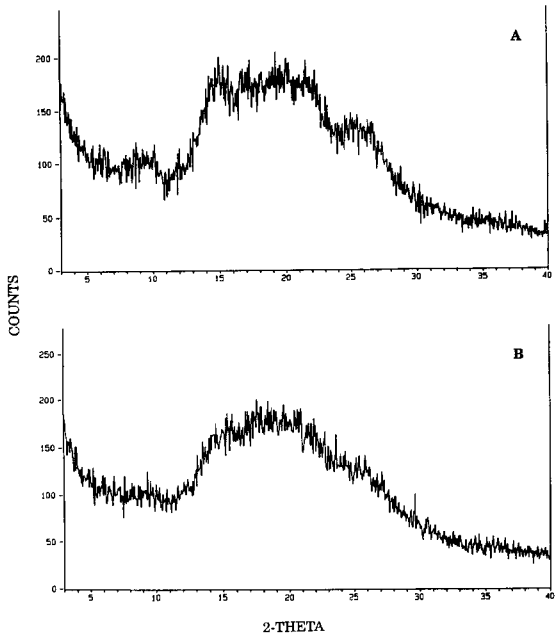

Fig. 2. X-ray diffraction pattern of Kapton® H polyimide film: (A) unirradiated and (B) irradiated to 3.1×10^{22} n/m^2.

Fig. 2a and b show the structure of the unirradiated and irradiated Kapton® H, respectively. In the unirradiated condition, crystalline peaks are superimposed on the broad amorphous peak confirming a partial crystalline structure of the Kapton® H. Preparation of Kapton® H polyimide films by the process of chemical conversion results in the structure consisting of a mixture of the amorphous phase (approximately 75%) and crystalline phase (approximately 25%). This is achieved by adding acetic anhydride to the polymer solution, along with a tertiary amine. As shown in Fig. 2b, irradiation effectively reduced the intensity of crystalline peaks in the X-ray diffraction pattern of Kapton® H, thus producing a more disordered structure. The irradiation-induced disordering (i.e., amorphization) of partially crystalline or fully crystalline structures has been demonstrated in other material systems as well, most notably in ceramics (see, for example, Ref. [4]).

3.2. Dynamic viscoelasticity

The dynamic viscoelasticity measurements were carried out in order to determine a possible shift in the glass transition temperature (T_g) with neutron irradiation. The extent of structural changes induced by irradiation and the corresponding changes in mechanical properties, may be inferred from the measured shift in T_g. The samples were heated at a constant heating rate of 2°C/min. The shift in T_g as a function of neutron fluence was determined from the shift in peak temperature in the corresponding tan δ curves, at the measurement frequency of 1 Hz. The values of T_g as a function of neutron fluence are shown in Table 1. In the unirradiated condition, the T_g of Kapton® H and HA is 392 and 414°C, respectively. These high values of T_g indicate excellent thermal stability of Kapton® polyimide films. While both Kapton® HA and H experience an increase in T_g under irradiation, the increase in T_g is substantially higher in Kapton® H. For comparison, the 4 K fast-neutron and gamma irradiation to the neutron fluence of 3.1×10^{22} n/m^2 increased the T_g of S2-glass-epoxy composite from 131 to 159°C (see Table 2 in Ref. [5]).

An increase in T_g from 414 to 418°C in the amorphous Kapton® HA is significant and it may be attributed to structural changes consisting predominantly of crosslink formation. Crosslinking causes greater restraints and decreases mobility of amorphous chain segments. The thermal barrier to segmental motion is increased, requiring a higher temperature for achievement of glass transition.

Kapton® H experienced a much larger increase in T_g during irradiation, namely, from 392 to 418°C. As shown in Section 3.1, irradiation disordered the partially crystalline Kapton® H structure. The increase in T_g from 392 to 418°C in Kapton® H may be therefore attributed to the processes of the irradiation-induced disordering and the irradiation-induced crosslinking.

3.3. FT-IR spectrometry

Table 2 shows the results of infrared spectrometry on unirradiated and irradiated Kapton® HA and H polyimide films. For the majority of the infrared bands, the absorption frequencies have been determined by operating the FT-IR microscope in the transmission (T) mode. The absorption frequencies of a few strong absorption bands could not be resolved in the transmission mode and have been therefore obtained in the ATR mode of the microscope operation. The infrared bands have been assigned based on the available data for the unirradiated Kapton® polyimide films [6]. The structural formula of Kapton® HA and H is shown in Fig. 3.

The absorption band at 3490 cm^{-1} can be assigned to the bonded O–H from absorbed water alone rather than

Table 1
Effect of low temperature fast-neutron and gamma irradiation on the glass transition temperature (T_g) of Kapton® HA and H polyimide films

Polyimide type	Neutron fluence n/m^2 ($E>0.1$ MeV)	T_g (°C)
Kapton HA	unirradiated	414
Kapton HA	3.1×10^{22}	418
Kapton H	unirradiated	392
Kapton H	3.1×10^{22}	418

Table 2
Absorption wavenumbers (cm^{-1}) in the FT-IR spectra of the unirradiated and irradiated (3.1×10^{22} n/m^2) Kapton® HA and H polyimide films

Kapton HA unirradiated (cm^{-1})	Kapton HA irradiated (cm^{-1})	Kapton H unirradiated (cm^{-1})	Kapton H irradiated (cm^{-1})
3491.5 T	3490.1 T	3485.9 T	3487.3 T
		3092.7 T	3093.2 T
3076.7 T	3075.9 T		
		3056.8 T	3057.3 T
1777.9 T	1778.1 T	1776.9 T	1777.8 T
1717.9 ATR	1718.9 ATR	1715.5 ATR	1715.8 ATR
1598.2 T	1598.4 T	1600.4 T	1660.2 T
1503.3 T	1502.2 T	1500.4 ATR	1500.8 ATR
1455.6 T	1455.9 T	1455.6 T	1455.8 T
1380.1 T	1378.5 T	1376.7 ATR	1377.8 ATR
1248.9 T	1246.0 T	1245.0 ATR	1245.3 ATR
1170.0 T	1169.8 T	1168.5 T	1169.7 T
1116.9 T	1116.4 T	1115.1 ATR	1115.9 ATR
1093.2 T	1093.1 T	1094.7 T	1094.9 T
1015.6 T	1515.3 T	1014.3 T	1015.0 T
882.9 T	882.5 T	884.5 T	883.9 T
822.2 T	822.7 T	821.7 T	822.7 T
725.1 T	725.2 T	726.3 T	726.3 T

partially from alcohol functional group in Kapton®. The hydrogen bonded O–H stretching frequency of the alcohol functional group appears generally in the frequency range of 3500 to 3200 cm^{-1}.

Infrared bands at 3077 cm^{-1} (Kapton® HA) and 3093 cm^{-1} (Kapton® H) can be attributed to the aromatic C–H stretch. The aromatic C–H stretching frequencies can be observed in the frequency range of 3200 to 3000 cm^{-1}. The differences between Kapton® HA and H may reflect structural subtleties associated with crystalline versus amorphous regions and the fact that H is anisotropic and whereas HA is isotropic.

IR band at 1778 cm^{-1} has been assigned to the bond stretching frequency of C=O of imide. The bands at 1718 cm^{-1} (Kapton® HA) and 1716 cm^{-1} (Kapton® H) have been similarly attributed to C=O of imide. The absorption bands of carbonyl groups are the most intense bands in the IR spectra of Kapton® HA and H and are generally observed in the 1800 to 1600 cm^{-1} region.

All of the absorption bands from about 1600 cm^{-1} through 725 cm^{-1} have been assigned to substituted phenyl.

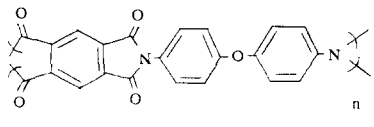

Fig. 3. Structural formula of Kapton® HA and H.

As shown in Table 2, the irradiated Kapton® HA and H show no new absorption introduced when compared to the unirradiated condition. Furthermore, none of the absorption bands observed in the unirradiated samples is missing in the IR spectra of irradiated Kapton® HA and H. Shifts on the order of 1.0 cm^{-1} or smaller can be observed in some peak locations after irradiation, however. They are indicative of changes in structure and consisting of disruptions in crystallinity and molecular weight.

Polyimides are nitrogen-carrying, condensed aromatic ring systems. The aromatic ring is an electron withdrawing group which makes resonance possible between the ring and the nitrogen. This, in turn, increases the radiation resistance of the structure by increasing its resonant energy. These structural features, in addition to CO functional group and the general presence of multiple bonds throughout the polymer backbone, help explain the enhanced radiation resistance of polyimides, especially when compared to epoxies [7].

3.4. Tensile testing

The engineering stress-strain curves of the unirradiated Kapton® HA and H polyimide films showed characteristic regions, namely, linear elastic region, parabolic work hardening region, linear work hardening region and fracture. The data on engineering stress and strain, as derived from these curves, are shown in Tables 3 and 4. Two values are included for each property measured in order to demonstrate reproducibility of the testing method used. The sub-size tensile specimens have been used to obtain these data (see Section 2.5 for a description of testing procedures). Nevertheless, the obtained values for tensile modulus, fracture strength and total strain at fracture of the unirradiated Kapton® HA, for example, are in a reasonable agreement with the results of conventional testing. The following values [8] have been reported for Kapton® HA by using procedures specified by the ASTM D-882-91:

Table 3
Tensile properties of the unirradiated and irradiated (3.1×10^{22} n/m^2) Kapton® HA polyimide films

Kapton HA	Unirradiated	Irradiated
Yield strength, 5% total strain	64.2 MPa 70.4 MPa	92.5 MPa 90.4 MPa
Fracture strength	188.4 MPa 170.4 MPa	138.7 MPa 131.1 MPa
Total strain at fracture	97% 83%	29% 27%
Tensile modulus	2.1 GPa 2.2 GPa	2.8 GPa 2.7 GPa
Vickers hardness	22.7	28.0

Table 4
Tensile properties of the unirradiated and irradiated (3.1×10^2 n/m^2) Kapton® H polyimide films

Kapton H	Unirradiated	Irradiated
Yield strength, 5% total strain	83.5 MPa	106.9 MPa
	84.2 MPa	110.4 MPa
Fracture strength	178.0 MPa	114.5 MPa
	191.8 MPa	110.4 MPa
Total strain at fracture	74%	7%
	76%	5%
Tensile modulus	2.6 MPa	–
	2.5 MPa	–
Vickers hardness	27.7	31.5

tensile modulus (2.1 GPa), fracture strength (207.0 MPa) and total strain at fracture (83%). In addition to tensile data, Tables 3 and 4 include the results of Vickers hardness measurements.

Low temperature fast-neutron and gamma irradiation has not changed the general features of the stress–strain curve for Kapton® HA. There is, however, a 20% increase in the elastic modulus and yield strength at 5% total strain (see Table 3). At the same time, the fracture strength decreased about 20% and the total strain at fracture was reduced to one-third of the unirradiated value. The Vickers hardness of the irradiated Kapton® HA increased about 20%.

The extent of radiation-induced hardening, as evaluated from tensile testing, was significantly larger in Kapton® H than in Kapton® HA polyimide films. As shown in Table 4, yield strength at 5% strain increased by 30% in Kapton® H. On the other hand, fracture strength decreased about 40% while the total strain at fracture dropped below 10%. The Vickers hardness of Kapton® H increased about 15% after irradiation.

Tensile properties of irradiated Kapton® polyimide films had been studied by other research groups (see Ref. [9] for a review). It has been shown [10] that reactor irradiation at 5 K to the fast-neutron fluence of 3.3×10^{21} n/m^2 does not change the tensile strength of Kapton® films as measured at 77 K. It has not been specified, however, whether the tested films were HA or H type. Kapton® H had been also irradiated at room temperature with 14 MeV neutrons and cobalt-60 gamma rays [11]. Fracture strength dropped to one-third of the unirradiated value at the neutron fluence of 1.6×10^{22} n/m^2. At the same time, total elongation at fracture dropped to less than one-eighth of the unirradiated value. It has been shown that 14 MeV neutrons are about eight times more effective than cobalt-60 gamma rays in producing mechanical property change [11].

Polyimide structure incorporates multiple bonds along the backbone of the polymer chain. This results in high irradiation resistance since most of the backbone of the repeat unit has two covalent bonds which must be broken to break the chain. It has been suggested that the radiation hardening of Kapton® H is related to the breaking of the main chain of the polymer [11]. By comparing the relative effects of 14 MeV neutrons and gamma rays on the degree of hardening of Kapton® H, it has been assumed that atomic displacements by high energy neutrons contributed significantly to the breaking.

In the present low temperature reactor irradiation of Kapton® HA and H polyimide films, approximately half of the total dose resulted from energy deposited from fast-neutrons and half from gamma rays. Tensile testing showed that irradiation to 3.1×10^{22} n/m^2 increases the tensile modulus and yield strength at 5% strain of both the Kapton® HA and H (tensile modulus of Kapton® H is not included in Table 4, however, because of a large scatter of data). The increase in tensile modulus and yield strength (or, equivalently, hardness) indicate that crosslink formation may be the predominant mechanism responsible for the observed radiation hardening [12]. This is consistent with the results of dynamic viscoelasticity measurements shown in Section 3.2. Furthermore, the increase in T_g was shown to be larger in Kapton® H than in Kapton® HA. In analogy to viscoelasticity measurements, the total strain at fracture (a measure of the extent of radiation hardening) was lower in Kapton® H as compared to Kapton® HA.

3.5. Monitoring the irradiation-induced property changes

As shown in this paper, low temperature fast-neutron and gamma irradiation induces changes in structure and mechanical properties of polyimide films. A technique has been sought that would permit monitoring structural changes and the resultant deterioration of mechanical and physical properties under irradiation and would be suitable for in situ monitoring of the performance of polyimide films under ITER operating conditions. Such a potential technique has been recently developed by researchers at MIT [13]. The method is called impulsive stimulated thermal scattering (ISTS). It is a real-time, noncontact, nondestructive in situ thin-film characterization technique.

By using the ISTS technique, elastic moduli, thermal diffusivities and the degree of structural order of the unirradiated and irradiated Kapton® HA and H polyimide films have been determined [14]. The results of these measurements are consistent with the results presented in this paper on the nature and the extent of radiation hardening of Kapton® HA and H polyimide films. Specifically, the increase in acoustic damping rate measured by the ISTS technique was shown to be proportional to the degree of radiation hardening of Kapton® HA and H as evaluated from the total strain at fracture in the present work.

Consequently, the ISTS technique would be suitable for monitoring the radiation-induced hardening of polyimide films during the fusion reactor operation.

4. Summary

Structure, chemistry and mechanical properties of the Kapton® HA and H polyimide films have been studied after their exposure to fast-neutron and gamma irradiation at a target temperature of 4 K. The fast ($E > 0.1$ MeV) neutron fluence was 3.1×10^{22} n/m^2. The gamma dose and the total dose were 3.6×10^7 and 6.7×10^7 Gy, respectively.

It has been shown by X-ray diffraction that the structure of Kapton® HA remained amorphous under irradiation. On the other hand, irradiation disordered the partially crystalline structure of Kapton® H as evidenced by the reduced intensity of crystalline peaks.

Irradiation increased the glass transition temperature of Kapton® HA and H, indicating that structural changes during irradiation consist predominantly of crosslink formation. The increase in T_g was significantly larger in Kapton® H.

FT-IR spectrometry showed that irradiation does not introduce any new absorption in Kapton® HA and H. Shifts in some peak locations have been observed, however. Other experiments are being planned in order to study the fundamental damage mechanisms in Kapton® polyimide films. An understanding of damage mechanisms would allow one to further optimize the performance of these materials under irradiation and perhaps design improved backbone structures.

Tensile testing showed that irradiation increases modulus and yield strength of both Kapton® HA and H. This is consistent with the proposed crosslink formation as the predominant mechanism of radiation hardening. By comparing the total strains at fracture, the extent of radiation hardening was shown to be significantly larger in Kapton® H. Since there is no significant difference in the postirradiation electrical strength constant of Kapton® HA and H, Kapton® HA would be the preferred candidate barrier material based on the radiation hardening criterion.

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