ELSEVIER

Journal of Nuclear Materials 246 (1997) 256–259

journal of nuclear materials

Letter to the Editors

Photothermal/photoacoustic method for in situ evaluation of radiation-hardened polyimide films

Randy Logan [a], A.A. Maznev [a], Keith A. Nelson [a,*], Janez Megusar [b]

[a] Department of Chemistry, Massachusetts Institute of Technology, Room 6-232, Cambridge, MA 02139, USA
[b] Materials Processing Center, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received 4 March 1997; accepted 3 April 1997

Abstract

A non-contact, non-destructive method is used to determine viscoelastic and thermal transport properties of a DuPont Kapton film before and after neutron irradiation to determine the changes that would be expected to occur in a nuclear reactor environment. The results demonstrate general capabilities for in situ, non-destructive evaluation (NDE) of radiation-induced material degradation. The specific application demonstrated is evaluation of insulation materials to be used in a superconducting magnet design in the International Thermonuclear Experimental Reactor (ITER). © 1997 Elsevier Science B.V.

1. Introduction

Magnets used to confine plasma in fusion reactors will experience extreme operating conditions. The magnets are operated at 4.2 K and are exposed to high fluences of fast-neutron and gamma irradiation as well as shear and compressive forces. The sensitivity of the magnet insulation material to these operating conditions is a critical feature of the magnet performance. In particular, degradation of the mechanical properties of magnet insulation upon fast-neutron and gamma irradiation must be assessed throughout the projected 25 year lifetime of the magnet. One such magnet insulation is a hybrid consisting of a barrier or coating in combination with vacuum-pressure impregnation and pre-preg primary insulation [1]. The barrier layer in this hybrid system can be a polyimide film. In this study, a novel characterization method was used to assess the degradation of the mechanical properties of the polyimide barrier material upon irradiation. Furthermore, it is shown that this characterization tool could be used as a non-contact, non-destructive monitoring device providing continuous feedback of the insulation material performance over the lifetime of the magnet.

Impulsive stimulated thermal scattering, or ISTS, is an all-optical method for noncontact, non-destructive, real-time measurement of mechanical and physical properties of thin film materials [2–4]. Two subnanosecond excitation laser pulses are spatially and temporally crossed at the surface of an absorbing sample to form an optical interference or 'grating' pattern. Optical absorption and sudden spatially periodic heating give rise to thermal expansion and acoustic responses at the grating wavevector. The wavevector is a function of the crossing angle and the wavelength of the excitation light pulses. The thermal and acoustic responses of the material cause a spatially periodic modulation or 'ripple' of the sample surface and can be monitored through time-dependent diffraction of a quasi-cw probe beam.

2. Experimental

The ISTS experimental setup has been described elsewhere [2] and is shown in Fig. 1. Frequency-tripling of the output of a Q-switched, mode-locked and cavity-dumped Nd:YAG laser yields 355 nm excitation pulses of 100 ps

* Corresponding author. Tel.: +1-617 253 1423; fax: +1-617 253 7030; e-mail: kanelson@mit.edu.

PII S0022-3115(97)00090-1

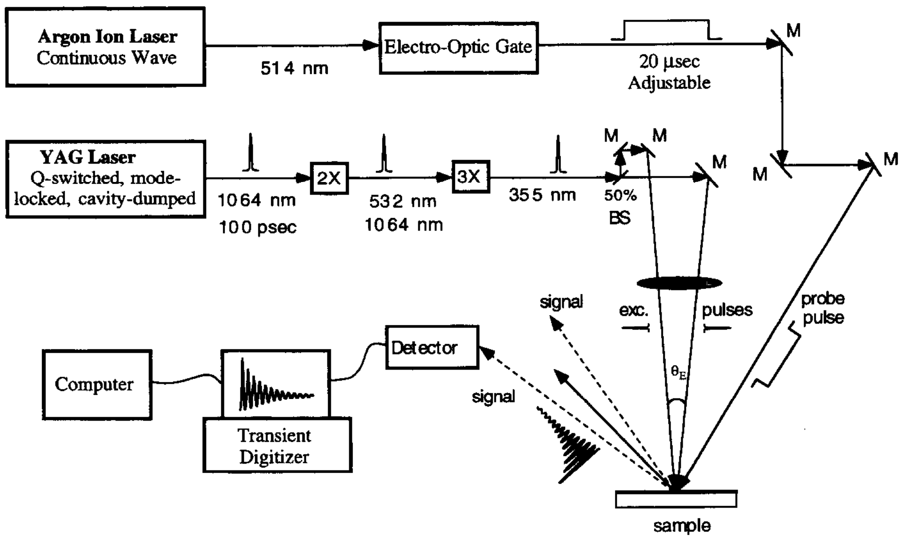

Fig. 1. ISTS experimental setup for thin films.

duration with 10 μJ of energy. This wavelength matches the red edge of the polyimide electronic absorption spectrum, and strong absorption leads to efficient heating. The pulses are split with a 50% reflector and recombined at the surface of the sample at an excitation angle, θ_E, which was 3.39 in this study. The probe beam is the electro-optically gated output of a cw single-mode argon ion laser which produces 1 W at 514 nm with a flat intensity profile. The gate gives rise to a quasi-cw square pulse with an adjustable temporal window. The diffracted signal is detected in reflection mode and temporally analyzed using a high-bandwidth amplified photodiode and digitizing oscilloscope.

Two DuPont polyimide samples, Kapton H and Kapton HA [5] films of 12.5 mm diameter and 0.25 mm thickness, were used. The films were held at 4.2 K and irradiated in a nuclear reactor with a fast-neutron fluence ($E > 0.1$ MeV) of 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. Irradiated films and unirradiated control samples were examined with ISTS in order to determine the effects of irradiation on the films and on the ISTS signal.

3. Results and discussion

Typical data from irradiated and unirradiated Kapton H are shown in Fig. 2. The data shown are the average of 500 single-laser-shot data scans and were collected in 5 seconds. Fig. 2a shows acoustic oscillations which gradually damp away on nanosecond time scales. Fig. 2b shows the same data on a microsecond time scale and a logarithmic signal intensity scale. The long-time signal is due to steady-state thermal expansion which washes away due to thermal diffusion from the peaks to the nulls of the grating. The data can be fit to the following expression [2]:

$$I(t) \propto |\Delta\rho(t)|^2 = \left[A e^{-\Gamma t} - B e^{-\gamma t} \cos(\omega t) \right]^2, \qquad (1)$$

where $\Delta\rho$ is the peak-null density excursion. This represents the square of the material displacements giving rise to diffraction. The first term describes the steady-state thermal expansion response with amplitude A and thermal diffusion rate Γ, and the second term describes the transient acoustic response with amplitude B, acoustic damping rate γ, and acoustic frequency ω. A fourier transform of the data in Fig. 2a is shown in Fig. 2c. This figure shows that the acoustic responses of the film before and after irradiation are dominated by a single mode at approximately 150 MHz. From the acoustic information provided through ISTS, sound velocities and elastic and loss moduli can be determined. From the thermal decay rate, the thermal diffusivity can be deduced.

There are three distinct differences between data from the irradiated and unirradiated samples. Fig. 2b reveals a significant increase in the thermal decay time (or a decrease in the thermal diffusion rate) upon irradiation. Fig. 2c shows a shift toward higher acoustic frequency and damping rate upon irradiation. Fig. 3 shows the results for Kapton HA, which exhibits the same three trends. Table 1 summarizes the effects of irradiation on acoustic frequency, thermal decay rate and acoustic damping rate of Kapton H and HA as derived from these figures.

Previous studies of radiation-induced effects in Kapton have been performed using X-ray diffraction, dynamic viscoelasticity, and tensile testing measurements [6]. X-ray diffraction reveals that irradiation leads to disordering of the partially crystalline Kapton H structure while the structure of Kapton HA remains amorphous under irradiation.

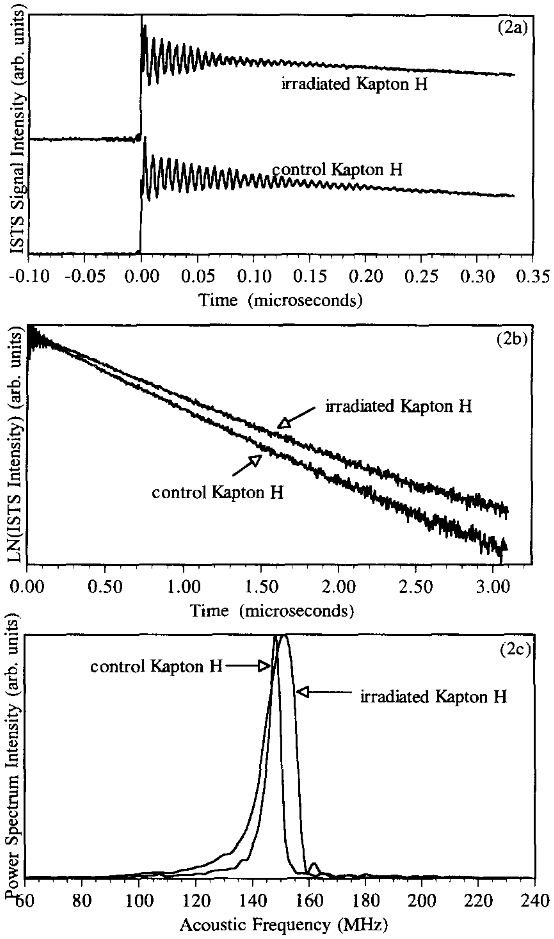

Fig. 2. (a) ISTS signal of Kapton H on short time scale showing acoustic oscillations. (b) ISTS Signal of Kapton H on long time scale showing thermal decay. (c) Power spectra of Kapton H samples.

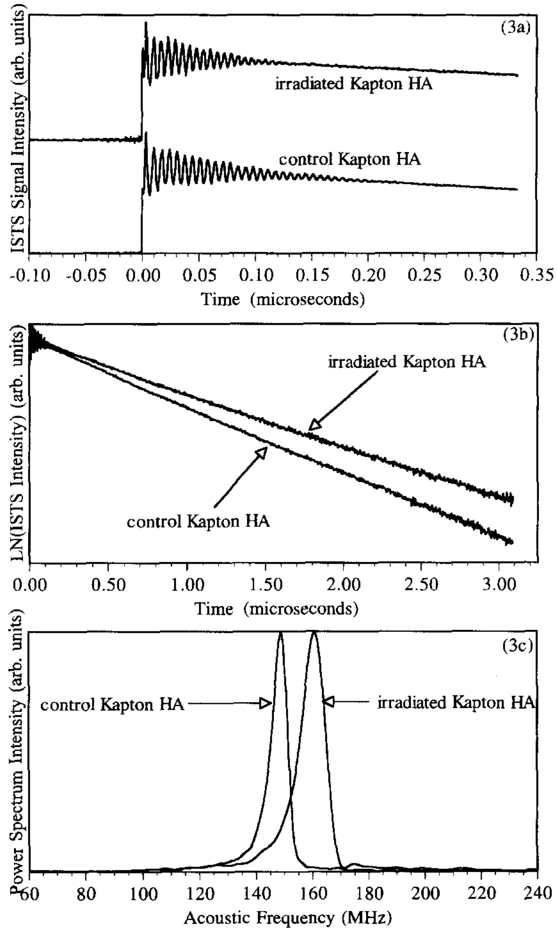

Fig. 3. (a) ISTS signal of Kapton HA on short time scale showing acoustic oscillations. (b) ISTS Signal of Kapton HA on long time scale showing thermal decay. (c) Power spectra of Kapton HA samples.

Dynamic viscoelasticity measurements show that in both Kapton H and HA, the glass transition temperature T_g increases following irradiation, with the change in Kapton H being much larger than in Kapton HA. The increase in T_g indicates that structural changes during irradiation consist predominantly of crosslink formation. Crosslinking causes greater constraints among the molecules and decreases the mobility of amorphous chain segments. Mechanical testing shows that irradiation increases tensile modulus and yield strength of both Kapton H and HA. These results are consistent with the hypothesis that crosslink formation as opposed to bond scission is the main damage mechanism during irradiation. Irradiation decreases the total strain to fracture of both Kapton H and

Table 1
ISTS data obtained from Kapton H and HA polyimide films before and after irradiation. Note: Data in table are the averages of 10 spots per sample. Error shown is ± 1 standard deviation

Status	Material	Acoustic frequency $\omega/2\pi$ (MHz)	Thermal decay rate, Γ (1/ms)	Acoustic damping rate, γ(1/ms)
Control	Kapton H	148.3 ± 0.4	0.96 ± 0.07	15.3 ± 0.8
Irradiated	Kapton H	151 ± 3	0.78 ± 0.04	34 ± 6
Control	Kapton HA	149.2 ± 0.5	0.95 ± 0.10	17.2 ± 1.0
Irradiated	Kapton HA	159 ± 2	0.79 ± 0.05	27 ± 4

HA. The reduction of total strain to fracture (a measure of radiation-induced hardening) is shown to be larger in Kapton H than in Kapton HA.

The ISTS results showing an increase in acoustic frequency in both Kapton H and HA upon irradiation indicate an increase in modulus, consistent with the earlier conclusions. The increase in acoustic damping rate in Kapton H and HA can be explained in terms of increased disorder which results in increased scattering of acoustic waves. As shown in Table 1, the increase in acoustic damping rate and the corresponding increase in disorder is higher in Kapton H than in Kapton HA upon irradiation. This result is consistent with the earlier conclusions that total strain to fracture, as a measure of radiation-induced hardening, is larger in Kapton H than in Kapton HA. Accordingly, the acoustic damping rate as measured by ISTS can be used to monitor in situ the extent of radiation-induced structural disorder and the resultant radiation-induced hardening of polyimide films. The thermal decay rate (see Table 1) decreases comparably in both Kapton H and HA upon irradiation. Since thermal diffusion occurs through acoustic phonon propagation, reduced thermal diffusivity is consistent with stronger acoustic damping and increased disorder that result from irradiation.

4. Conclusions and future work

ISTS permits rapid, non-invasive determination of changes in viscoelastic and thermal properties caused by irradiation in a nuclear reactor. ISTS data for Kapton polyimide films are consistent with those of more conventional testing methods such as X-ray diffraction, dynamic viscoelasticity, and mechanical testing. ISTS measurements of the type presented here are now routine and ISTS instruments are available commercially. The technique could be used for in situ evaluation of the changes that occur to the neutron irradiated magnet insulation materials. The specific application demonstrated here is currently under development for the international thermonuclear experimental reactor (ITER). Other systems exist, such as the LHC Project at CERN, where the superconducting magnets are the most critical item. While these and other applications may experience radiation damage from sources other than neutrons, the need still exists for in situ evaluation of radiation-induced damage. Previously, ISTS measurements have been performed on ceramic [7] and metallic [8] materials as well as polymers, opening up the possibility that ISTS may also be able to evaluate insulation materials other than Kapton, such as alumina coatings or mica.

Acknowledgements

This work was supported in part by NSF Grant No. DMR-9317198. R.L. acknowledges an NSF Graduate Fellowship.

References

[1] J.B. Schultz, R.P. Reed, Advances in Cryogenic Engineering, Vol. 40 (Plenum, New York, 1994) pp. 985–992.
[2] J.A. Rogers, K.A. Nelson, J. Appl. Phys. 75 (1994) 1534.
[3] A.R. Duggal, J.A. Rogers, K.A. Nelson, J. Appl. Phys. 72 (1992) 2823.
[4] J.A. Rogers, K.A. Nelson, J. Polym. Sci. B34 (1996) 861.
[5] R. Srinivasan, R. Hall, W. Loehle, W. Wilson, D. Albee, J. Appl. Phys. 78 (1995) 4881.
[6] J. Megusar, J. Nucl. Mater. 245 (1997) 185.
[7] Y. Yang, K.A. Nelson, F. Adibi, J. Mater. Res. 10 (1995) 41.
[8] R. Logan, A.A. Maznev, K.A. Nelson, J.A. Rogers, M. Banet, Materials Research Society Symposium Proceedings, 1997, to be published.