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Deformation behavior of ion-irradiated polyimide

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We study nanoindentation hardness, Young's modulus, and tensile strength of polyimide (Kapton H) films bombarded with MeV light ions in the predominantly electronic stopping power regime. Results show that, for all the ion irradiation conditions studied, bombardment increases the hardness and Young's modulus and decreases the tensile strength. These changes depend close-to-linearly on ion fluence and superlinearly (with a power law exponent factor of ~ 1.5) on electronic energy loss. Physical mechanisms of radiation-induced changes to mechanical properties of polyimide are discussed.

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Polyimides are high-performance plastic materials with an attractive combination of properties, including low electrical conductivity, high tensile strength, and stability at temperatures as high as 400 °C.[1] The most common commercially available (aromatic) polyimide has the DuPont trade name Kapton. The chemical formula of Kapton is $(C_{22}H_{10}N_2O_5)_n$, and the structure of its repeat unit consists of two imidic rings, two carbonyls, and three phenyl rings, two of which are connected by an oxygen ether link. Effects of ion bombardment on various properties of polyimides, and Kapton in particular, have attracted significant research efforts for the past two decades.[2] Most investigations have focused on electrical and optical properties since Kapton exhibits a very large increase in electrical conductivity and optical density as a result of irradiation.[2–7]

Mechanical properties of ion-irradiated polyimide have been a subject of few previous studies.[2] In particular, Lee and co-workers[2,8] have shown that the nanoindentation hardness of Kapton increases after irradiation with different ion species. They have provided compelling evidence that such an irradiation-induced increase in hardness is due to the effects of electronic (rather than nuclear) energy loss processes of energetic ions.[2,8] In addition, Hill and Hopewell[9] have demonstrated that tensile strength of Kapton decreases after irradiation with 3 MeV ^{1}H ions, which have a rather low value of the electronic stopping power (~ 1.6 eV/Å).[10,11]

However, we are not aware of any systematic studies of the effects of ion irradiation conditions on the major mechanical properties of polyimides such as elastic (Young's) modulus, hardness, and tensile strength, describing the three major modes of deformation — elastic and plastic deformation and fracture. In particular, the dependence of mechanical properties of polyimides on the electronic energy loss of energetic ions is not well understood. Knowing such a dependence, however, is crucial for choosing ion irradiation conditions to achieve desirable mechanical properties of the irradiated material. There is also a very limited (and often controversial) understanding of the atomic-level physical mechanisms responsible for radiation-induced mechanical changes in polymers.[2,3] In this paper, we show how irradiation with MeV light ions affects hardness, Young's modulus, and tensile strength of Kapton. Our results reveal that the efficiency of changing mechanical properties is a superlinear function of the electronic energy loss of light ions.

TABLE I: Ion irradiation conditions used in this study. In all cases, irradiation was done at room temperature. Calculated valued of the projected ion range (R_p) as well as electronic [$(dE/dx)_e$] and nuclear [$(dE/dx)_n$] stopping powers are also given. These calculations were done with the TRIM code.[10,11]

Ion	Energy (MeV)	R_p (μm)	Flux (10^{11} cm^{-2} s^{-1})	$(dE/dx)_e$ (eV/Å)	$(dE/dx)_n$ (10^{-3} eV/Å)
^{1}H	1.5	36.4	13	2.57	1.65
^{4}He	3.8	19.5	5	14.3	10.0
^{12}C	3.5	4.57	2	109	233

The 12-μm-thick free-standing Kapton H films used in this study were obtained from DuPont Co. The 4 MV ion accelerator (NEC, model 4UH) at LLNL was used for ion bombardment. During irradiation, the incident beam axis was aligned normal to the film surface. All experiments were done at room temperature although the precise temperature of Kapton films during bombardment could be higher due to ion-beam heating effects. Table I gives the details of the ion irradiation conditions used.

After irradiation, all samples were subjected to indentation using a UMIS-2000 nanoindentation system with an ~ 4.3 μm radius diamond spherical indenter. For indentation, each sample was mounted on a stainless steel stub using a mounting wax heated to ~ 100 °C. The shape of the indenter tip was characterized by scanning electron microscopy. The indentation system and indenter tip were carefully calibrated by indenting fused silica.

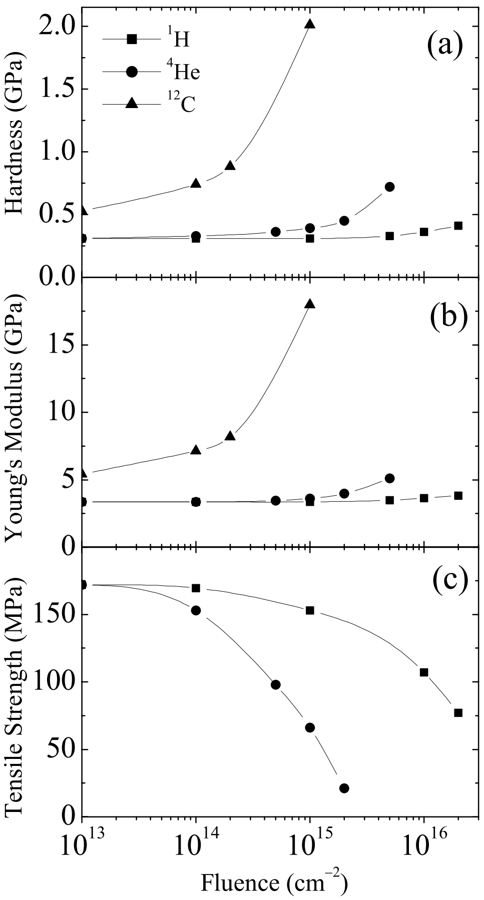

FIG. 1: Ion-fluence dependencies of nanoindentation hardness (a), Young's modulus (b), and tensile strength (c) after irradiation with MeV ^{1}H, ^{4}He, and ^{12}C ions. See Table I for the details of irradiation conditions.

A series of both partial and continuous load–unload indents was carried out. All indents were performed at room temperature. The partial load–unload data were analyzed using the method of Field and Swain[12] to extract the hardness and elastic modulus as a function of indenter penetration. An Instron tensile testing instrument was used to measure the tensile strength of ^{1}H- and ^{4}He-irradiated samples; i.e., in cases when ions penetrated through the entire 12-μm-thick Kapton film. For tensile test studies, films were laser-cut into dog-bone shapes prior to ion bombardment.

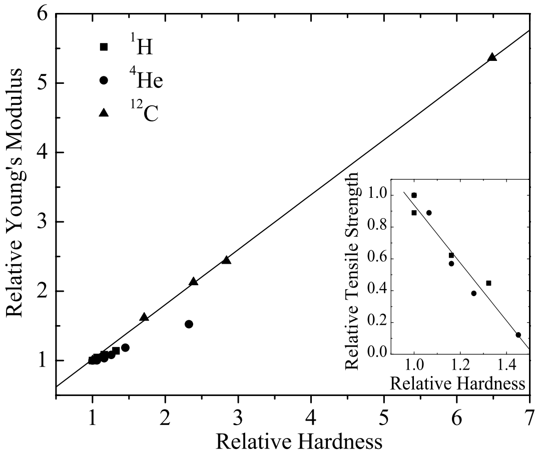

FIG. 2: Dependence of relative hardness on relative Young's modulus for irradiation with MeV ^{1}H, ^{4}He, and ^{12}C ions. Inset: The dependence of relative tensile strength on relative hardness.

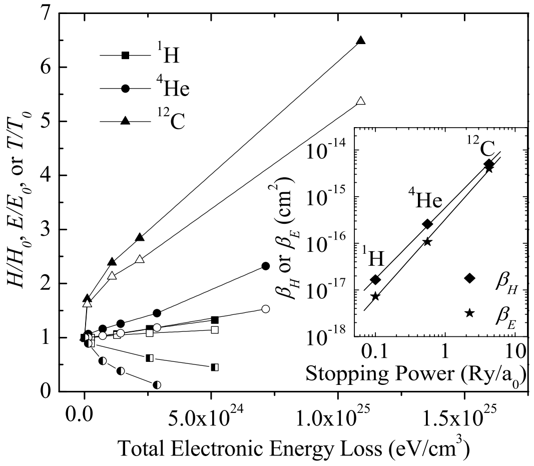

FIG. 3: Dependencies of relative hardness (open symbols), relative Young's modulus (closed symbols), and relative tensile strength (half filled symbols) on the total electronic energy loss deposited (defined as the stopping power times fluence). The inset shows the dependence of parameters β on the electronic energy loss for the three ion species studied. See the text for details.

Figure 1 shows ion-fluence dependencies of hardness, H, [Fig. 1(a)], Young's modulus, E, [Fig. 1(b)], and tensile strength, T, [Fig. 1(c)] of Kapton bombarded with ^{1}H, ^{4}He, and ^{12}C ions.[13] It is seen from Fig. 1 that, for all the three ion species, bombardment results in an increase in both H and E, with a corresponding decrease in T. Figure 1 also shows that, with increasing ion mass [and the stopping power (see Table I)], the changes in mechanical properties are observed for lower ion fluences.

Figure 2 shows the dependence of the relative Young's modulus (E/E_0) on relative hardness (H/H_0), where H_0 and E_0 are the values for virgin (unirradiated) Kapton. It is seen from Fig. 2 that E/E_0 depends essentially linearly on H/H_0. The best linear fit to ^{12}C data, shown as a solid line in Fig. 2, has a slope of 0.79 ± 0.01. In addition, the inset in Fig. 2 shows that relative tensile strength (T/T_0) decreases close-to-linearly with increasing relative hardness (and Young's modulus), with a slope of -1.82 ± 0.18. Figure 2, therefore, reveals that ion irradiation results in a larger increase in H than in E, while irradiation-induced changes to T are nearly twice more rapid than those to H or E.

Figure 3 shows the dependencies of H/H_0, E/E_0, and T/T_0 on the total electronic energy loss, defined as the electronic stopping power [i.e., $(dE/dx)_e$ given in Table I] times ion fluence. It is seen from Fig. 3 that radiation-induced changes to mechanical properties do not simply (linearly) scale with the total electronic energy loss. Indeed, Fig. 3 shows that, for any given value of the total electronic energy loss, irradiation with different ion species results in rather different values of H, E, or T.

Figure 3 also shows that, particularly in the case of ^{1}H and ^{4}He ions, H and E depend close-to-linearly on the total energy loss (and, thus, on ion fluence). Hence, ion-beam-induced changes to H can be approximately described as $H/H_0 = 1 + \beta_H \Phi$, where Φ is ion fluence, and β_H is a parameter describing the efficiency for changing H by ion irradiation under given conditions. This parameter, as well as similar parameters β_E and β_T, can be determined from linear fits of ion fluence dependencies of H, E, and T shown in Fig. 1.

It should be noted that slight nonlinearity of ion fluence dependencies, revealed in Fig. 3, particularly for the case of ^{12}C ions, is not unexpected. Indeed, Fig. 1 shows that, even in the case of ^{12}C ions, ion fluences resulting in measurable changes in H and E are $\gtrsim 10^{13}$ cm^{-2}. Calculations based on the well-known track/cascade overlap model[14] show that $\sim 8\%$ and 50% of the surface area is covered with ion tracks with a diameter of 10 Å (which is not an unreasonable diameter of tracks produced by 3.5 MeV ^{12}C ions) for ion fluences of 10^{13} and 10^{14} cm^{-2}, respectively. Hence, considerable track overlap occurs for all the three ion species studied for the ion fluences used, giving rise to slight nonlinearity of ion-fluence dependencies.

The inset in Fig. 3 shows a double-logarithmic dependence of parameters β_H and β_E on the electronic stopping power (in Ry/a_0, where Ry is Rydberg, and a_0 is Bohr radius). It is seen from this inset that β_H and β_E can be expressed as power law functions of the electronic stopping power: $\beta_{H,E} \propto (dE/dx)_e^{n_{H,E}}$. Least square fits to experimental points in the inset in Fig. 3, shown as solid lines, give $n_H = 1.52 \pm 0.04$ and $n_E = 1.68 \pm 0.06$. This result indicates that the efficiency for changing mechanical properties of polyimides is a *superlinear* function of electronic energy loss, at least in the range of the electronic stopping powers investigated in the present study (i.e., $\sim 3 - 109$ eV/Å).[15] Hence, irradiation with UV, x-rays, or energetic electrons (with much lower densities of electronic excitation than in the case of MeV ions) is considerably less efficient for changing mechanical properties of polyimides as compared to the case of MeV ion bombardment.

The superlinearity of changes to H and E on electronic energy loss revealed in this work can be understood as follows. Changes in hardness upon ion irradiation have been attributed to the formation of cross-links (covalent bonds) between different polymer chains.[2] Such cross-links form as a result of the reconstruction of bonds broken by intense irradiation-induced electronic excitations in *adjacent* polymer chains. Since this process requires that broken bonds are created in adjacent chains, the efficiency of cross-linking is expected to depend nonlinearly on the excitation density (i.e., on the electronic stopping power), in agreement with our experimental results. However, additional studies are currently needed to better understand atomic-level mechanisms of such cross-liking along ion tracks as well as the contribution and mechanisms of irradiation-induced chain scission in polyimides.

In conclusion, results have shown that ion irradiation increases the hardness and elastic modulus and decreases the tensile strength of polyimides. These changes depend close-to-linearly on ion fluence and superlinearly on electronic energy loss. Results of this study may have important implications for the estimation of mechanical properties of polyimides for given ion irradiation conditions.

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