

Depth-Dependent Hardness Improvements in Ion Irradiated Polystyrene (*Example A*)

Gopal R. Rao¹ and Eal H. Lee (*Example B*)

Metals and Ceramics Division, Oak Ridge National Laboratory, (*Example C*)

Oak Ridge, TN 37831-6376, U.S.A.

¹Materials Research Society, 506 Keystone Drive,
Warrendale, PA 16066, U.S.A.

ABSTRACT (*Example D*)

Polystyrene (PS) was irradiated with 2 MeV He⁺ ions to a fluence of 3.3×10^{19} ions/m². A cross-section of the irradiated layer was subjected to hardness measurements across the section using a nanoindentation technique. Results showed that hardness increased as a function of irradiation depth and showed a maximum value of 12 GPa at a depth of approximately 6.5 μm, for a total ion penetration range of 9 μm, as compared to a hardness of 0.45 GPa for unirradiated PS. The hardness variation with depth followed the trend for Linear Energy Transfer (LET) for ionization from the energetic ions to substrate atoms. This investigation showed for the first time how hardness varies as a function of depth for ion-irradiated polymers; this variation approximately follows the ionization LET profile, suggesting that cross-linking in the polymers could be proportional to ionization.

INTRODUCTION (*Example D*)

Ion irradiation of polymers can have a significant effect on surface-related properties [1,2]. In particular, recent studies at Oak Ridge National Laboratory have shown that ion irradiation can dramatically improve surface-mechanical properties of polymers such as hardness and tribological properties [2-4]. Since the modified layer thickness is of the order of a few micrometers, surface hardness has been characterized using a depth-sensing nanoindentation technique. Thus far, hardness values at 100 nm depth have been reported as a standard for comparison in order to minimize subsurface as well as substrate effects [5]. However, hardness measurements in ion implanted polymers are complicated by the fact that the hardness of the material varies as a function of depth within the modified layer due to a nearly Gaussian distribution of deposited energy, which produces a depth-dependent variation in microstructure. In the present study, a cross section of the irradiated polymer layer was subjected to hardness measurements across the section, in order to examine hardness variation as a function of irradiation depth, and to correlate the variation with energy deposition mechanisms. In addition, optical microscopy and atomic force microscopy were used to image the indents.

EXPERIMENTAL DETAILS (*Example G*)

Polystyrene (PS), obtained from Dayton Plastics (Dayton, Ohio) in the form of 100 μm thick film was irradiated with 2 MeV He⁺ to a fluence of 3.3×10^{19} ions/m². Helium with an energy of 2 MeV was used since the penetration depth is around 9 μm, yielding a thicker modified layer than for a higher mass ion. Also, fluences higher than 1×10^{19} ions/m² have yielded significant

improvements in hardness of polystyrene. The irradiation was performed at the triple ion irradiation facility in the Metals and Ceramics Division at Oak Ridge National Laboratory [6], using a 2.5 MV Van de Graaff accelerator. The specimen was cut and mounted edge-on in epoxy resin. The surface was then polished using fine diamond paste (successively with 6 μm , 3 μm and 0.25 μm diamond particle sizes) thus yielding a cross-section of the irradiated layer.

Hardness measurements were performed using the Nanoindenter⁷ (NanoInstruments, Knoxville, Tennessee) [5]. Indents were made at 10 μm intervals along a path that was inclined approximately 6° to the epoxy-polystyrene interface intersection with the plane of the polished surface, starting in the epoxy, into the irradiated layer and terminating in the unirradiated PS substrate. For each indent, a 20 mN load was used and the total indentation depth was 500 nm with hardness values reported for a 100 nm depth. The distance along the path was converted into equivalent normal depth from the epoxy/polystyrene, and the results are reported in terms of hardness as a function of irradiation depth. The indents were subsequently imaged using optical microscopy and scanning force microscopy (SFM). SFM was conducted using a Topometrix⁷ Explorer Scanning Force Microscope.

DISCUSSION

Hardness values as a function of irradiation depth are shown in figure 1. Hardness increased from a value of 0.4 GPa for the epoxy to a high of 12 GPa for a depth of around 6.5 μm , before dropping to a value of 0.45 μm for the unirradiated PS beyond the 9 μm ion range (see table I). The variation in hardness was not smooth as shown in the figure. For comparison, the hardness at 100 nm depth, measured while indenting normal to the irradiated surface, was 3.32 GPa. The series of indents is shown in the

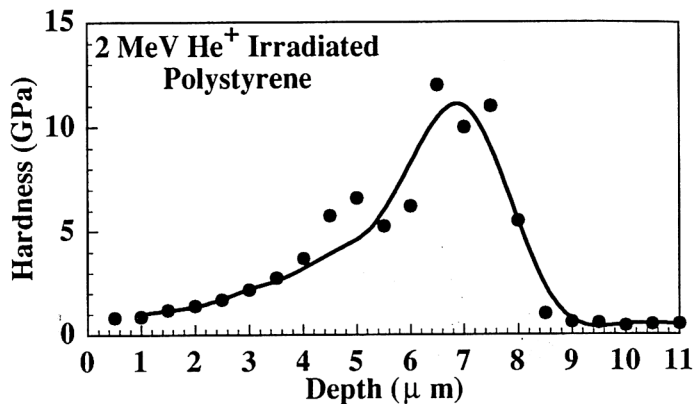


Figure 1. Nanoindentation hardness values as a function of irradiation depth (data points) taken across the cross-section showing a peak hardness of 12 GPa at a depth of approximately 6.5 μm . (*Example E*)

Table I. Hardness vs depth values obtained using nanoindentation. (*Example E*)

Depth (μm)	Hardness (Gpa)
0	0.4
6.5	12
9	0.45

composite optical micrograph, which distinctly shows the irradiated layer between the epoxy and the underlying unirradiated PS. The epoxy-polystyrene interface can be seen as a dark line. The residual images of the indents, however, were not visible within the irradiated polymer layer. Scanning force microscopy also did not show indents within the modified region.

It is to be noted that the irradiated layer does not appear to be flat but seems to have the appearance of a "hill" with the peak, corresponding to the white band at a depth within the irradiated layer cross-section corresponding approximately to the maximum hardness. This is probably due to the fact that since this region of higher hardness is cross-linked to a greater extent, it was more resistant to the polishing treatment. This "hill-like" surface contour is also responsible for the larger scatter in hardness values in figure 1 where the indenter penetrated the material on the slopes of the "hill" causing only partial penetration.

Hardness can be defined as resistance to indenter penetration, or as the average pressure under the indenter, calculated as the applied load divided by the projected area of contact incorporating the plastic component of displacement. In fact, the hardness of the material increases as the plastic depth of penetration decreases, for a given load. In this study, no residual indents were observed within the irradiated layer which corroborates the significant hardness improvements shown in figure 1. In a separate experiment, a comparatively high load of 120 mN at a rate of 1000 mN/s was used to indent unirradiated and irradiated PS. An SFM image of these indents indicates the significant plastic deformation in pristine PS as opposed to the much smaller deformation observed within the harder irradiated layer.

Cross sectional line analysis (*Example K*)

A cross sectional line analysis through the indents, performed on the computer using the SFM scan data, indicated that the residual plastic indentation depth was around 420 nm for the unirradiated PS and around 40 nm for the implanted region corresponding to ratio of 10:1. For the indents, the depth of the indents in the unirradiated region were estimated to around 30 nm. Again assuming a ratio of 10:1, the depths of indents in the implanted region would be on the order of a few nm explaining why they were not visible in the optical micrographs.

Surface hardness (*Example K*)

It has been shown that linear energy transfer (LET) mechanisms can be correlated with surface hardness for ion implanted polymers [7]. Impinging energetic ions lose their energy to substrate atoms mainly through inelastic collisions causing ionization, and by nuclear recoils causing displacements. For ion irradiation of polymers, ionization likely causes cross-linking thereby

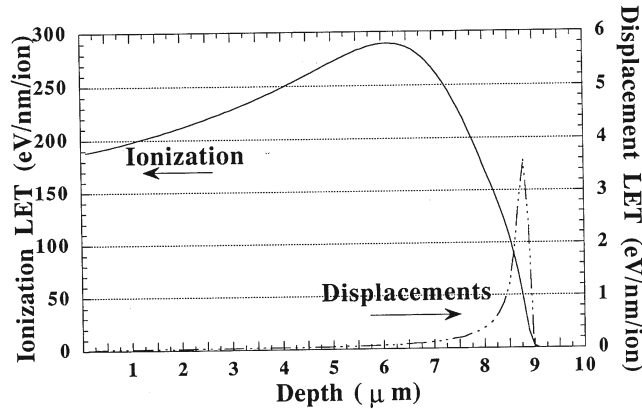


Figure 2. Ionization and displacement Linear Energy Transfer (LET) profiles for 2 MeV He⁺ irradiation of polystyrene. The peak of the ionization profile corresponds to the peak hardness depth for the cross-sectional nanoindentation measurements in figure 2. (*Example E*)

increasing hardness, whereas recoils are believed to cause chain scissions which are detrimental to hardness improvements [7]. LET values for ionization and recoils in the case of 2 MeV He⁺ irradiation of PS are shown in figure 2. Comparing LET values with hardness as a function of depth in figure 1, it is evident that the hardness variation with depth has the same trend as ionization, and in fact the peak of the ionization plot occurs at around 6.5 μm which corresponds to the peak depth for hardness. This gives additional support to the thesis that ionization is a significant factor for cross-linking, which is believed to be ultimately responsible for hardness improvements [8]. See equations 1.

$$E \sim 1/M_C \tag{1}$$

(Example F)

Where E is Young's modulus, M_C is the average molecular weight, H is the hardness, and the ratio (h/a) is a residual impression parameter.

It is interesting to note that hardness values at lower irradiation depths (up to around 2 μm) are still low, even though ionization LET values are high. This can at least partly be attributed to the effect of the epoxy and interface. Beneath the indents, the strain field volume is fairly large, typically ten times the indent volume approximately, and the indents near the interface will be influenced by the presence of the adjacent epoxy material due to the lateral dilation of the softer epoxy. Thus, the actual hardness is somewhat underestimated due to the presence of the epoxy. The hardness values also drop to lower values around the 8 to 9 μm irradiation depth range more quickly than the ionization LET values. This again may be due to the fact that at depths in this range, hardness measurements are affected by the lateral dilation of the adjacent unirradiated polystyrene. As seen in figure 4, displacement LET is insignificant when compared to ionization LET for He which is a very light ion, hence very few scissions are expected. In spite of these uncertainties, it is evident that hardness values follow a similar trend as ionization LET, as a function of depth. Additional studies are necessary to investigate mechanisms for the depth dependence of hardness.

CONCLUSIONS (*Example H*)

This study for the first time shows how hardness varies with depth in ion irradiated polymers. In addition, it was shown that ionization LET followed a similar trend as hardness, as a function of depth, which was most likely related to cross-linking. Ion irradiation of polymers has a significant effect on mechanical properties such as hardness and the present study shows that property improvements can be predicted and possibly tailored using knowledge of basic mechanisms.

ACKNOWLEDGMENTS (*Example I*)

The authors would like to thank Drs. S. J. Zinkle and M. B. Lewis for discussions and critical review of the manuscript. Research supported by the U.S. Department of Energy, Division of Materials Sciences under contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems Inc. One of the authors (GRR) was supported through the ORNL Postdoctoral Research Program administered jointly by Oak Ridge National Laboratory and Oak Ridge Institute for Science and Education.

REFERENCES (*Example J*)

1. T. Venkatesan, L. Calcagno, B. S. Ellman and G. Foti, "Ion Beam Effects in Organic Molecular Solids and Polymers," *Ion Beam Modification of Insulators*, ed. P. Mazzoldi and G. W. Arnold (Elsevier, 1987) pp.301-379.
2. E. H. Lee, M. B. Lewis, P. J. Blau, and L. K. Mansur, *J. Mater. Res.* **6**, 610 (1991).
3. G. R. Rao, E. H. Lee and L. K. Mansur, *Wear* **162-164**, 739-747 (1993).
4. G. R. Rao, E. H. Lee and L. K. Mansur, *J. Mater. Res.* **10**, (1995) (in press).
5. E. H. Lee, Y. Lee, W. C. Oliver, and L. K. Mansur, *J. Mater. Res.* **8**, 377 (1983).
6. M. B. Lewis, W. R. Allen, R. A. Buhl, N. H. Packan, S. W. Cook and L. K. Mansur, *Nucl. Instrum. Meth.* **B43**, 243 (1989).
7. E. H. Lee, G. R. Rao, M. B. Lewis and L. K. Mansur, *Journal of Materials Research* **9**, 1043 (1994).
8. E. H. Lee, G. R. Rao, M. B. Lewis and L. K. Mansur, *Nucl. Instrum. Meth.* **B74**, 3326 (1993).
9. W.J. Weber, J.L. Bates, C.W. Griffin, and L.C. Olsen in *Defect Properties and Processing of High Technology Nonmetallic Materials*, edited by Y. Chen, W.D. Kingery, and R.J. Stokes, (Mater. Res. Soc. Proc. **60**, Pittsburgh, PA, 1986) pp. 235-242.