# CHARACTERIZATION OF SUB MICRON MECHANICAL BEHAVIOR AND FRACTURE PROCESSES OF POLYMERS AND BIOMATERIALS

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## ABSTRACT

This paper will present the use of novel methods to study submicron mechanical behavior and fracture mechanisms in medical grade polymers and in biological materials. Ultra small angle x-ray scattering (USAXS) is used to detect defects at both the nanometer and micrometer size scale in polymers due to cyclic loading. This study examines the effects of crosslinking on both the initiation of fatigue damage and the inception of crack growth in orthopedic polymers. USAXS is used to measure and quantify the flaw size distribution and its evolution due to fatigue loading. Nanoindentation is used to quantify local elastic properties due to morphological changes and as a function of crosslink density of the polymer. Another use of sub-micron indentation is the characterization of mechanical properties of biological materials. This work provides an insight into the mechanical behavior of medical polymers and biological materials at the submicron scale.

## INTRODUCTION

Fracture and mechanically induced failure remains a prevalent problem in the medical industry. An example of this problem is found in orthopedics and is especially prevalent in polymeric total knee replacements where articulating contact stresses cause damage accumulation and subsurface crack propagation resulting in premature failure due to biological complications. Numerous studies have characterized the fatigue crack propagation behavior of these orthopedic grade ultra high molecular weight polyethylene (UHMWPE) resins but the mechanisms of flaw nucleation *in vivo* remains elusive. This paper will present the use of novel methods to study fatigue mechanisms in UMWPE. Ultra small angle x-ray scattering (USAXS) is used to detect defects in UHMWPE due to fatigue loading at both the nanometer and micrometer size scale. The effect of crosslinking on both the initiation of fatigue damage and the inception of crack growth in medical grade UHMWPE is examined. USAXS is used to measure and quantify the flaw size distribution and its evolution due to fatigue loading [1]. This study shows that the degree of crosslinking alters the evolution of cyclic damage in UHMWPE and its subsequent resistance to crack initiation and propagation.

Submicron-scale nanoindentation experiments are utilized in order to examine the effect of crosslink density and intrinsic polymer morphology on the local mechanical properties of polyethylene. Indentation is an effective tool for nano and microscale mechanical characterization. Indentation theory relies on the assumption that when a rigid indenter deforms a material, the initial unloading curve represents purely elastic recovery. The depth of penetration and applied load can be continuously monitored, and corrections can be made for large displacements in order to determine the local hardness and elastic modulus from the unloading portion of the indentation curves.

While submicron indentation or nanomechanical characterization has broad applicability in the thin film and hard disk industry, it has only recently been shown to be effective for mechanical characterization of softer materials, including both biological and polymeric materials [2].

An additional focus of this work is the use of nanoindentation for the mechanical characterization of vascular tissues and constituents of artherosclerotic plaques. Atherosclerosis is characterized by the accumulation of lipids, fibrous tissue, and calcifications in artery walls, which are collectively known as plaques. Failure of plaque via biological or mechanical activation can result in numerous medical complications. Plaque rupture is associated with release of debris into the bloodstream that can occlude downstream arteries, frequently resulting in stroke, heart attack, or death. While finite element models have been useful in modeling hemodynamic conditions *in vivo*, they have remained limited in their predictive capabilities due to the lack of available data on the actual material properties of the vascular wall or blood contacting plaques. Mechanical characterization of diseased vessels remains elusive due to the material complexity and heterogeneous nature of plaques and individual constituents. This paper addresses the use of nanoindentation methods to isolate the mechanical properties of different plaque constituents in vascular tissues.

## MATERIALS AND METHODS

Polyethylene was used as the base polymeric material for the fatigue study and USAXS characterization. Crosslinking was performed using gamma radiation and subsequent annealing was performed in an oven heated up to 150 C for 4 hours and then cooled slowly to room temperature. Three doses of gamma radiation were used to create different levels of crosslink densities in the polymer: 50 kGy, 100 kGy and 200 kGy. The samples were subjected to both fatigue crack propagation studies and stress-life analysis. For the crack propagation studies, the stress intensity range necessary to generate crack growth at a rate of $10^{-6}$ mm/cycle was measured and defined as $\Delta K_{incept}$. For the stress life fatigue tests, the number of cycles to the onset of yield were monitored as a function of nominal stress range. Tests were performed to determine a stress yield life over the range of 10-$10^5$ cycles. Small angle X-ray scattering, SAXS, was used to examine stress life specimens that were fatigued at a stress range below the yield life stress range. SAXS was performed at the Center for Materials Science and Engineering at MIT using a Rigaku rotating-anode CuK$\alpha$ source running at 40 kV and 30 mA. Scattered X-ray intensities, I, were obtained as a function of scattering vector, q.

For the nanoindentation analysis of the polymers, flat coupons with 1 cm x 1 cm surface areas were machined from the irradiated rod stock described above. For assessment of morphological effects, untreated LDPE and HDPE samples were also machined into coupons. Prior to indentation, all the samples were mechanically polished to an arithmetic mean roughness of less than 0.125 μm. Samples were ultrasonically cleaned and degreased with isopropanol prior to testing. Nanomechanical tests were performed using an atomic force microscope (AFM) retrofitted with a load-displacement transducer (Triboscope, Hysitron, Inc.). A spherical diamond tip with a radius of curvature ~20 μm was used to indent the samples. A relatively blunt tip was chosen in order to only compress the material under the tip, thus avoiding excessive deformation of the polymers. Indentations were performed by positioning the diamond tip over the sample surface, indenting to a specified maximum load (in the range of 75-600 μN) at a specified loading rate, holding at the maximum load for a few seconds, and then withdrawing the tip at the same rate. All the indentation experiments were performed at a constant loading/unloading rate of 30 μN/s.

Carotid plaque tissue was excised *en bloc* in routine endarterectomy surgeries at the San Francisco VA Hospital. Prior to mechanical characterization, all carotid plaques were analyzed using magnetic resonance imaging in order to determine the general composition of the vascular tissue. The diseased vascular tissue included intima and media, but not adventitia. The artery was sectioned into a calcified region of the external carotid artery (ECA), a fibrous region of the external carotid artery, and the less diseased common carotid artery (CCA).

The three sections of the carotid plaque were maintained in a formalin solution. An elastomeric Silastic replica of the carotid plaque was also characterized in order to provide a soft material standard for the study. All samples were tested using a Hysitron TriboScope transducer mounted on a Digital Instruments NanoScope E Scanning Probe Microscope. In indentation mode, the instrument is a load-controlled displacement-sensing device. A conospherical shaped diamond probe tip was used to do all of the mechanical properties testing and imaging of the samples. The radius of curvature of the probe tip was approximately 120 μm. Indentations with maximum loads of 50 μN to 800 μN were made in each of the samples using a standard trapezoidal loading function. The load was ramped linearly to the maximum load in 5-10 seconds, held at maximum for up to 10 seconds, and then unloaded linearly for 5 seconds. The applied load and the depth of penetration were continuously monitored. Corrections for large displacements were made, and the hardness (H) and the reduced modulus ($E_r$) were then calculated from the unloading curves. The reduced modulus is related to modulus of elasticity (E) by: $\frac{1}{E_r}=\frac{(1-\upsilon_1)^2}{E_1}+\frac{(1-\upsilon_2)^2}{E_2}$ , where the subscript 1 refers to the indenter material, the subscript 2 refers to the indented material, and ν is Poisson's ratio. For a diamond indenter tip, $E_1$ = 1140 GPa and $\nu_1$=0.07.

**RESULTS AND DISCUSSION**

The fatigue crack propagation results for the polyethylene groups are presented in Figure 1. It is apparent that radiation crosslinking results in decreased crack propagation inception value, $\Delta K_{incept}$, as compared to the non-radiated specimens. Also, the crack inception value continues to decrease as radiation dose or crosslink density is increased. The annealed UHMWPE also exhibited a similar $\Delta K_{incept}$ than the non-annealed UHMWPE but slightly different propagation behavior in Paris regime. The total-life fatigue behavior and the load histories of specimens used for SAXS analysis are shown Figure 2. The results presented in Figures 1 and 2 reveal that crosslinking is detrimental to crack propagation resistance but is beneficial to the initiation of a crack. Recent work [3] has shown that crosslinking limits modes of plasticity resulting in a decreased yield strength and post yield strain hardening. The limited plasticity reduces strain to failure in the polymer and results in a reduction of accommodated plasticity at the crack tip. The decreased plasticity at the crack tip enables more of the crack driving force to be utilized in crack propagation rather than dissipated through plastic work. One of the additional goals of this study was to use ultra-small angle X-ray scattering (USAXS) to assess the nucleation of small flaws or defects in the total life specimens. USAXS utilizes a scan range that allows for detection of structural changes on the order of microns, whereas conventional SAXS can only detect features up to hundreds of nanometers. The plots shown in Figure 2 were determined in order to understand where a safe loading range would be for the crosslinked polymers. It is believed that submicron sized flaws are generated even when cycling within the safe loading range. The conventional SAXS utilized in this study provided results that showed no difference between the fatigued and unfatigued specimens, as well as no insight as to structural changes on the micron size level. These findings, however, do not preclude morphological changes or damage at a submicron scale. Figure 3 shows the USAXS plot of intensity as a function of scattering vector for three gamma radiated specimens [4]. Two of the specimens were subjected to cyclic loads well below the stress-yield life curve for that material while one specimen remained unfatigued. As the number of fatigue cycles increased the scattering intensity increased due to structural changes induced by the fatigue process. The increase in intensity is likely due to the formation of micro flaws within the polymer. That is, while the total life specimens did not fracture they very likely contain very small defects than can eventually grow to a critical flaw size. Whether this lifetime exceeds the life expectancy of an orthopedic device has yet to be proven.

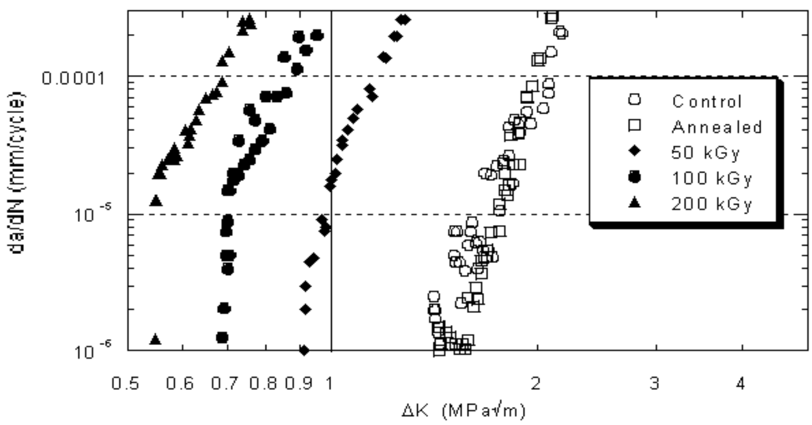



Figure 1. Results from the crack propagation tests for all five material groups.

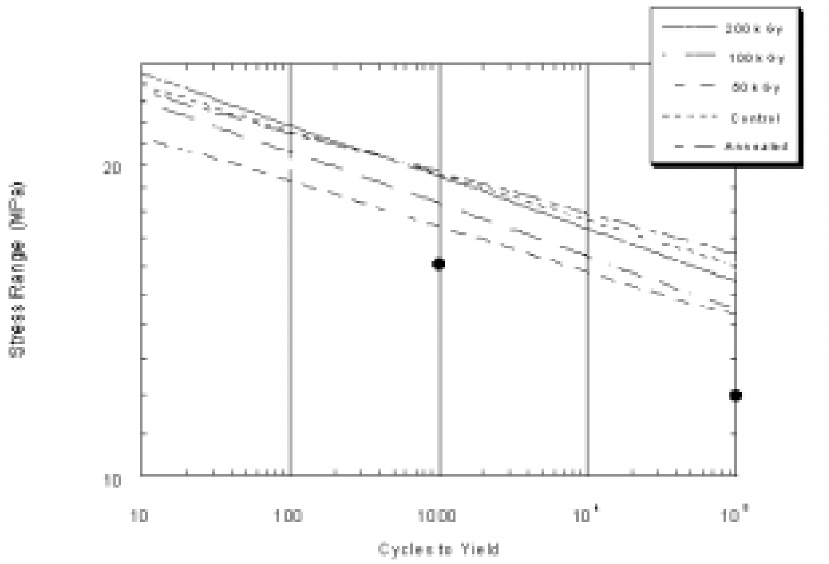



Figure 2. Stress-yield life plot for the five material groups. The markers denote the fatigue conditions subjected to the SAXS specimens.

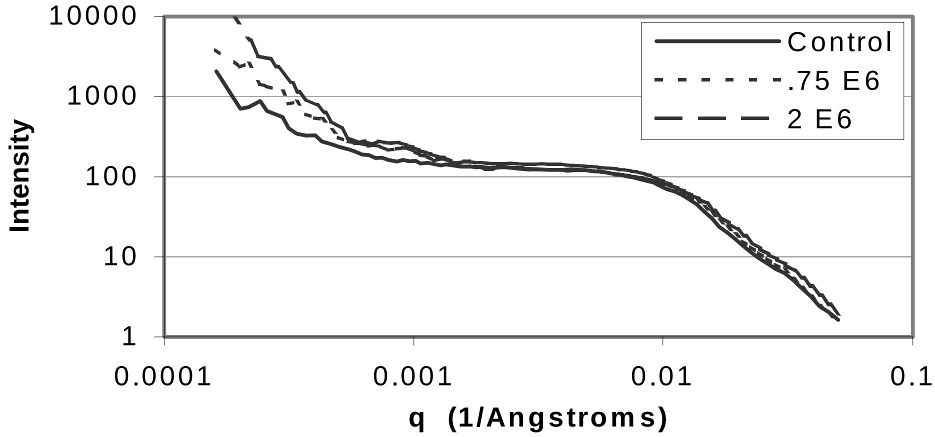



Figure 3. Plot showing the relative intensity of scattered X-rays as a function of scattering vector for gamma-air specimens [4]. Fatigue cycles noted in key.

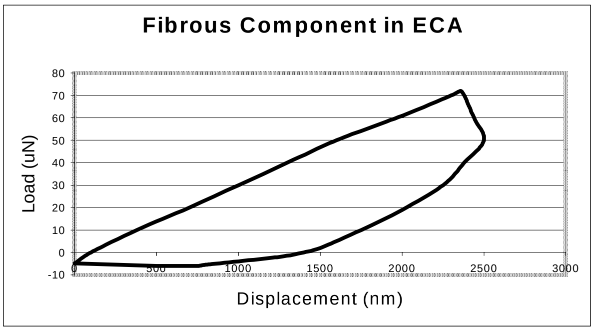
Elastic modulus and hardness values were determined from the indentation response of the polyethylene samples. Table 1 shows the average values of the mechanical properties obtained by nanoindentation unloading curves. For the UHMWPE samples, it is clear that the heat treatment, used as a control for the crosslinked resins, leads to both softening and reduction of the stiffness in comparison to the untreated rod stock. With the increase in crosslink density brought about through gamma radiation treatments at doses of 50 and 200 kGy, the resins exhibit a statistically higher elastic modulus, but with no detectable change in hardness. The sample radiated to a dose of 100 kGy is indistinguishable from the virgin rod stock. These results suggest that although radiation may increase the elastic stiffness of UHMWPE through the enhancement of the crosslink density, this stiffening effect may be counteracted by thermal softening effects resulting from the post radiation heat treatment.

For the morphological analysis, the HDPE exhibited the highest elastic modulus and hardness values, whereas LDPE had a higher elastic modulus and slightly higher hardness than the UHMWPE control materials. This is expected since the crystallinity of HDPE (78% crystalline) is significantly greater than those of UHMWPE (50% crystalline) and LDPE (30% crystalline) . While the molecular weight of UHMWPE (3-5 million) is much greater than that of HDPE (90,000) and LDPE (50,000), it is the crystalline phase that provides resistance to deformation. The fairly similar hardness and elastic modulus values of UHMWPE and LDPE may be due to their close match in crystallinity (50%) and density (0.93 g/mol).

**Table 1.** Measured nanomechanical materials properties of polyethylene.

| Material | Treatment | $E_r$ (MPa) | H(MPa) |
|---|---|---|---|
| UHMWPE | none | 611 ± 47 | 12.1 ± 1.5 |
| | 150°C, 4 h | 363 ± 67 | 5.6 ± 2.0 |
| | 50 kGy, 150°C, 4 h | 727 ± 53 | 12.0 ± 3.5 |
| | 100 kGy, 150°C, 4 h | 621 ± 42 | 11.7 ± 2.5 |
| | 200 kGy, 150°C, 4 h | 716 ± 50 | 12.3 ± 3.2 |
| LDPE | none | 709 ± 70 | 12.2 ± 2.8 |
| HDPE | none | 1330 ± 180 | 18.8 ± 4.3 |

The results of the nanoindentation analysis of the vascular plaques are shown in Figure 4 (A) and (B). These figures show load-displacement behavior of the fibrous and calcified region of the external carotid artery (ECA), respectively. The measured component properties are summarized in Table 2. These findings indicate that the calcifications in vascular tissue result in substantial increases in hardness and modulus. A limitation of this study is that the tissue was stored in formalin and tested in air. It is expected that hydrated tissue stored in physiological environments would result in more accurate values and would exhibit much lower moduli and hardness. The calcifications are expected to be less susceptible to the fixative and hydration, resulting in more accurate values for the calcified than the fibrous tissue. The nanoindention technique revealed a 50 fold increase in hardness for the calcified ECA over the CCA. The calcification resulted in a modulus 1000 times stiffer than adjacent fibrous tissue. The trends found in this study are quite promising. Future tests performed under physiological conditions will verify this behavior and will provide insight into the quantitative material properties of the vascular wall.

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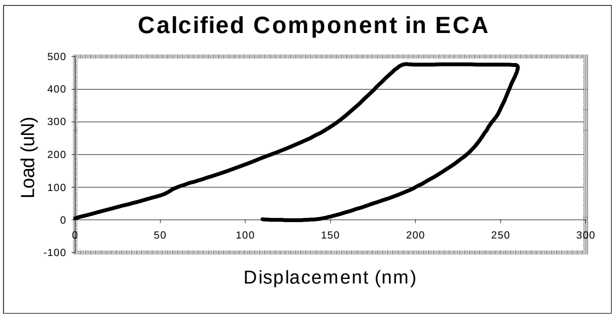


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**Figure 4:** Sample load-displacement behavior of (A) fibrous components of the ECA , and (B) calcified components of the ECA for formalin-fixed tissue [2].

**Table 2:** Reduced modulus ($E_r$) and hardness (H) values for silastic and formalin-fixed carotid tissue.

| Material | $E_r$ (MPa) | H (MPa) |
|---|---|---|
| Silastic | 0.36 | 0.03 |
| CCA | 0.99 | 0.05 |
| Fibrous ECA | 1.89 | 0.05 |
| Calcified ECA | 1156 | 2.58 |

## CONCLUSIONS

This study shows that USAXS can be used to detect small scale cracks nucleated in cyclic loading. Further this work shows that submicron-scale indentation is an effective technique for evaluating the surface mechanical properties of polymer materials and isolated consituents in vascular tissues.

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