1.1 Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is the current material of choice for bearing surface applications in total joint arthroplasty. In an effort to enhance the wear properties of the material many companies have recently resorted to electron beam and gamma irradiation of the components prior to the machining. It is of considerable interest to accurately determine the dose absorbed by the material, both in bulk and as a function of position, for quality control and process validation purposes. Several methods exist that yield information about the dose absorbed by the material. For instance, swell ratio testing, in which a crosslinked sample is swollen in a good solvent, will give the crosslink density and molecular weight between crosslinks assuming that the interaction parameter between the solvent and polymer is well-known. This technique will only give the volumetric-averaged crosslink density. Similarly, dynamic mechanical analysis (DMA) will give a qualitative measurement of volumetric crosslink density if a viscoelastic model is assumed. Both of these techniques can be used to infer the absorbed dose level by establishing a calibration curve between the cross-link density and the absorbed dose level. However, at high radiation dose levels (around 150kGy), the cross-link density of the polymer reaches a saturation level and the determination of dose beyond these levels becomes impossible. The advances in Fourier Transform Infrared Spectroscopy (FTIR), coupled with a greater understanding of the radiation chemistry of polyethylenes, have permitted the development of a powerful technique that indicates the radiation dose received by a sample at much greater accuracy than the swelling or the DMA techniques. The FTIR technique essentially makes use of an internal dosimeter in the polyethylene, which can be measured with a conventional FTIR or an ir-microscope to produce a *radiation dose index* (RDI).
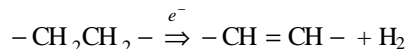
1.2 Dosimetry

Dosimetry, or the determination of the amount of radiation delivered to a material, is usually accomplished with photochromic dyes. Photochromic dyes typically contain ferrous sulfate, which undergoes an ionic change upon irradiation. These dyes change color when irradiated and accurate determination of the absorbed dose is attainable by comparing the color of the dye with calibration tables. These materials will saturate around 5 Mrads (50 Kgray), which is below the typical dose levels used in the biomedical area. Additionally, the dyes are not indicative of the radiolytic chemistry that occurs in the material. Consequently, these dosimeters have useful albeit limited application in the dose determination of irradiated UHMWPE.

1.3 FTIR Analysis

When polyethylene is irradiated, hydrogens are abstracted from the polymer backbone. Several competitive reactions can occur at the free radical left at the abstraction site, including crosslinking between two adjacent chains, formation of allyl radicals, and combination of two radicals along the same backbone to form a *trans*-vinylene group, the last of which is shown below.

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$$-CH_2CH_2- \overset{e^-}{\Rightarrow} -CH=CH- + H_2$$

It has been observed by several groups that this latter reaction scales very well with delivered dose up to approximately 1000 kGy, and can be represented by an empirical binomial equation. Furthermore, there is no evidence to suggest that the rate of formation of trans-vinylene groups in the crystalline region of the sample varies from the amorphous region.

By examining an *ir* absorbance peak associated with the vinylene group, it is possible to quantify the number of *trans*-vinylene groups produced per unit volume. The number of double bonds formed per 100 eV of absorbed energy is characterized by a *G* value, which is a function of the temperature, radiation source, material, etc. With FTIR, one can measure the presence of these double bonds with a high degree of accuracy. As the number of bonds are directly related to the absorbed dose of the material, the absorption peak at the frequency corresponding to these bonds provides a relative measurement of the absorbed dose in the sample.

Because FTIR is a line of sight measurement, the area under the characteristic absorbance peak will depend on the thickness of the sample. Consequently, the area of the vinylene peak is normalized with the area of the frequency corresponding to the methylene peak. This ratio is termed the *radiation dose index* (RDI), a dimensionless value indicative of the amount of radiation absorbed by the sample.
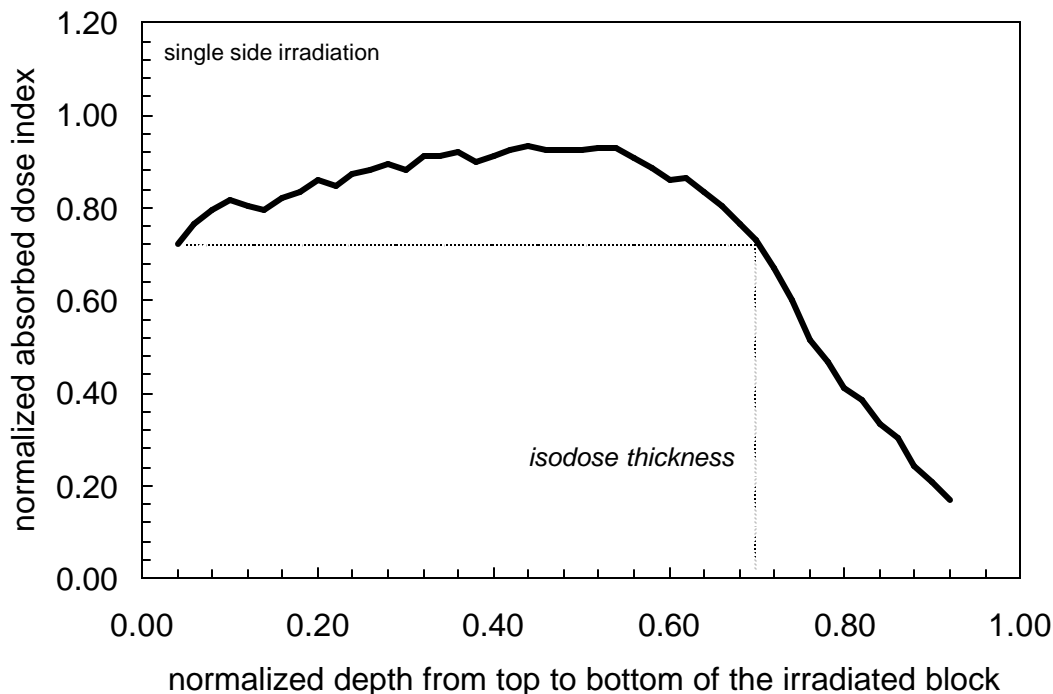
$$RDI = \frac{A_{C=C}}{A_{CH_3}} \times 100 \tag{1}$$

The advances in ir-microscopy permit profiling of samples across their thickness. By the use of lenses and aperture slits, the *ir* beam can be focused as small as 10 μm in diameter, allowing the *ir*-interrogation of a very small sample area. When the sample is mounted on a precision *x-y* table, the entire sample can be profiled in steps as small as 10 μm. This technique is often used to monitor the oxidation index, indicated by the carbonyl band, in irradiated samples. As will be shown below, micro FTIR is very useful in determining the uniformity of the RDI across the thickness of an irradiated sample.

1.4   Uses of RDI

1.4.1   Cascade Effect

Samples irradiated with high-energy electrons typically have an absorbed dose distribution similar to that shown in Figure 1. This distribution is due to the electron cascade effect. When incident electrons delivered from the electron beam source contact the surface of the sample, secondary electrons are abstracted from the polymer chains and are deflected into the sample. These secondary electrons in turn abstract tertiary electrons, until a cascade of electrons is flowing through the sample. Consequently, the maximum flux of electrons is not at the surface, but rather at a level below the sample surface. This characteristic distance is dependent on the chemical nature of the polymer, the energy of the electrons, and temperature. Some researchers will place overlays composed of metal or plastic on top of the sample, particularly thin samples, to obtain the maximum absorbed dose closer to the surface.

The absorbed dose shown in Figure 1 decays quickly after reaching a maximum. Often termed the isodose thickness, accurate knowledge of this value is critical when deciding what will be the maximum thickness of an irradiated component.
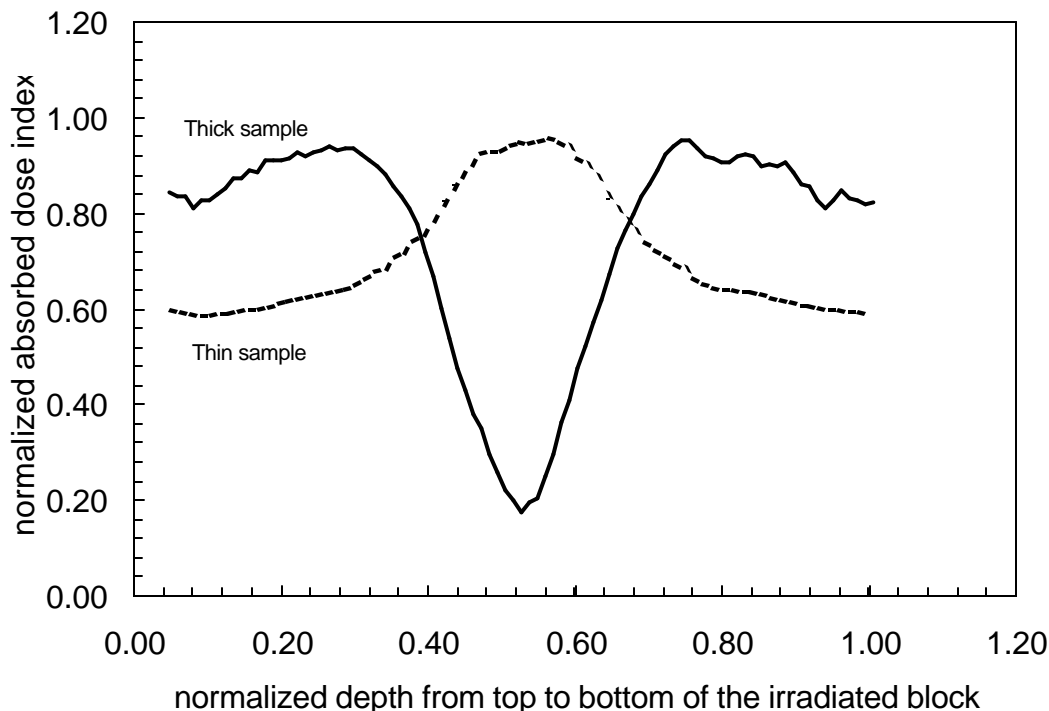
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Figure 1: **Cascade effect in a polyethylene sample irradiated in an electron beam on one side.**

To allow the use of thicker irradiated components, samples are often irradiated on both sides. The absorbed dose profile will be a spatial addition of the cascades from both sides of the sample. Depending on the thickness of the sample, the dose profile can vary significantly. In Figure 2, the radiation dose index for two samples of differing thickness that have been irradiated on two sides are compared. In these plots, the depth has been normalized with the sample thickness to allow better comparison. The width of the thicker sample is larger than twice the isodose thickness, and thus prevents overlap of the two cascades, yielding a region on the center of the sample that has received very little irradiation. In contrast, the thin sample experienced a strong overlap in the cascades from both sides, so that the center of the sample has received a much high radiation dose. Clearly, an optimal thickness exists that will yield a fairly uniform radiation dose profile, and RDI analysis can be used to determine this thickness

1.4.2   Quality control

The stability and reproducibility of the RDI analysis makes it an excellent technique for quality control and assurance. Cross-linked UHMWPE can be analyzed following the irradiation to determine the exact absorbed dose level. The *ir* analysis can be performed anytime following the irradiation process because the trans-vinyl species in polyolefins are quite stable in the long term. Similarly, shelf-aged or retrieved UHMWPE components can be analyzed years later to determine the exact sterilization doze and RDI uniformity. Additionally, no calibration is required for quality assurance measurements. A sample prepared under conditions that yield the desired properties (wear, mechanical response, etc.) can be analyzed with FTIR. Its RDI profile can then be used as a gold standard, to which all other samples are compared.
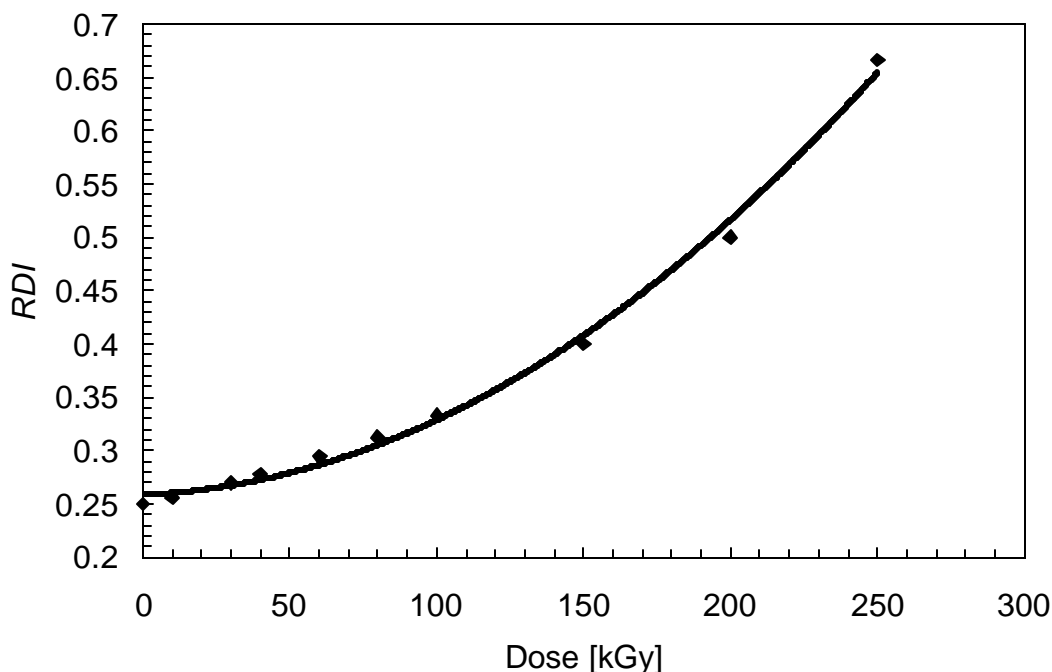
RDI analysis has been used previously as a quality assurance tool for the polyethylene component of balloon catheters used in angioplasty, and has been through FDA scrutiny.

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Figure 2:   Polyethylene samples irradiated on two sides with an electron beam. The sample depths are normalized with each sample thickness.

1.4.3   Calibration plot

If an absolute measure of absorbed dose is required, a master calibration curve can be prepared. An example of a master curve is shown in Figure 3. Samples that have been irradiated with known doses, quantified with photochromic dyes, are interrogated by FTIR to determine their RDI. A master curve, fit to a binomial or trinomial equation, will represent the radiolytic response of the material under the specific conditions used to prepare the curve (temperature, dose rate, oxygen content, etc.). Samples that have received an unknown dose under the same processing conditions can be compared to this curve, which will provide the dose absorbed by the material. A calibration curve is required for each type of processing conditions, as the analysis is sensitive to any factors that affect the *G*(vinyl).

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Figure 3: **Master plot of radiation dose index (RDI) as a function of radiation dose for polyethylene. At absorbed dose levels of 30 kGy and higher the first derivative of RDI with respect to dose becomes higher; therefore, dose determination is more accurate at higher doses unlike what is observed in the DMA technique and swelling analysis.**

1.4.4   Gamma Irradiation

The discussion thus far has centered on electron beam irradiation. This technique also has applicability to gamma irradiation. Gamma radiation is a deeper penetrating radiation source than electron beam, and has a smaller cascade effect. Additionally, it has been observed that the potential for errors in reported dose levels are higher with electron beam facilities than with gamma, given that the dose rate depends on the variation in belt speed, beam current, irradiation time, and width of beam. For this reason, more medical facilities are turning to γ-rays. The RDI analysis discussed in this application note will also work well with samples irradiated with γ-rays. Absolute measurements will require a calibration plot prepared from gamma-irradiated samples.