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Analytical Techniques for Assessing the Effects of Radiation on UHMWPE

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Introduction

The prevalence of the use of radiation chemistry for sterilization and improvement in wear behavior of ultra high molecular weight polyethylene (UHMWPE) has led to a suite of test techniques used to quantify dose yields, side products, and final morphological and mechanical properties. Some of these techniques have become standardized through ASTM or ISO committee evaluation, while others are still undergoing test scrutiny.

In UHMWPE processing, the manufacturer starts with the polyethylene in a powder form. The powder is consolidated, or molded, via ram extrusion, compression molding, or other less common techniques such as isostatic pressing. The form of the consolidated sample will be either a slab, bar stock, or implant pre-form. If crosslinking is desired, the manufacturer will subject the sample to ionizing radiation, either from a gamma source or an electron-beam source. Additional thermal processing often occurs to reduce free radical concentrations and subsequent oxidation. The implant is then machined from the irradiated stock, after which additional sterilization (gamma, e-beam, or ethylene oxide) occurs.

In this report, I summarize the common test techniques used in the industry today, and their use in analyzing the UHMWPE during the various stages of processing, including analysis of retrieved components.

Technique Summarization

The table below lists the common test techniques used today to characterize UHMWPE.

Morphology	Chemical	Mechanical	In Vitro
Transmission Electron Microscopy	Fourier Transform Infra-red Spectroscopy (ASTM 1421)	Small Punch [1]	Accelerated Aging
Scanning Electron Microscopy	Electron Spin Resonance Spectroscopy	Compression (ASTM D2990)	Wear Testing
Small Angle X-ray Analysis	Gel Permeation Chromatography (ASTM D6474)	Tensile (ASTM D2990, D638)	
Differential Scanning Calorimetry (ASTM D3417)	Dilute Solution Viscometry (ASTM D2857, F4020)	Fatigue (ASTM E647)	
	Swelling Analysis (ASTM D2765)	J-Integral (ASTM E813)	
	Sol-Gel (ASTM D2765)		

	Trace element (ASTM F648)		
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Morphology

Information about the UHMWPE chain structure before and after consolidation can be obtained through electron microscopy. The pre-consolidated powder may be analyzed with scanning electron microscopy (SEM), an example of which is shown in Figure 1. Modern SEM systems have greatly improved resolution compared to systems of years past, and morphology with size scales of 100 nm can be viewed easily. The samples are typically gold-coated and viewed with conventional SEM, although uncoated specimens may be examined with environmental SEM. Some loss of resolution usually results from the latter approach.

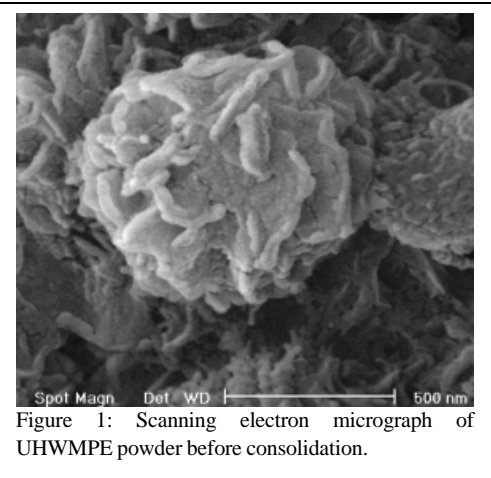


Figure 1: Scanning electron micrograph of UHMWPE powder before consolidation.

Changes in crystalline structure with consolidation and radiation-treatment can be viewed with transmission electron microscopy (TEM). As opposed to the surface analysis technique of SEM, TEM takes a spatial average of the polymer morphology, relying on differences in electron density to yield structure. Consequently, microtoming is required to yield 50-200 nm thick slices, which are then stained with chlorosulfonic acid to enhance contrast. An example of the ribbon-like lamellae found in UHMWPE is shown in Figure 2. This micrograph shows primary large lamellae, with smaller lamellae interspersed.

Small angle X-ray spectroscopy (SAXS) is a quantitative technique used to examine crystal spacing, crystal size, and lattice structure [2]. This technique is of particular use in

determining the effects of consolidation and wear on the crystalline structure on the surface and in the bulk of a sample.

Additional quantitative information about crystallinity, and how it changes with radiation treatment, can be obtained from differential scanning calorimetry (DSC). In this technique, a small sample of UHMWPE (typically 5-10 mg) is sealed in a aluminum sample chamber, then heated in a temperature sweep from ambient to 200°C at a specified rate, typically 10°C/min. By monitoring the heat flow required to maintain this temperature sweep, thermal events such as glass transitions and melting endotherms can be monitored.

A typical trace for UHMWPE is shown in Figure 3. The construction lines shown are used to determine the total heat of melting ΔH (the area under the endotherm), and the onset temperature of melting (extrapolated from the peak melting temperature). Knowing the total heat of fusion of UHMWPE ($\Delta H_f = 291$ J/g), the percentage of crystallinity is computed as

$$\% \text{ crystallinity} = \frac{\Delta H}{\Delta H_f} * 100\%$$

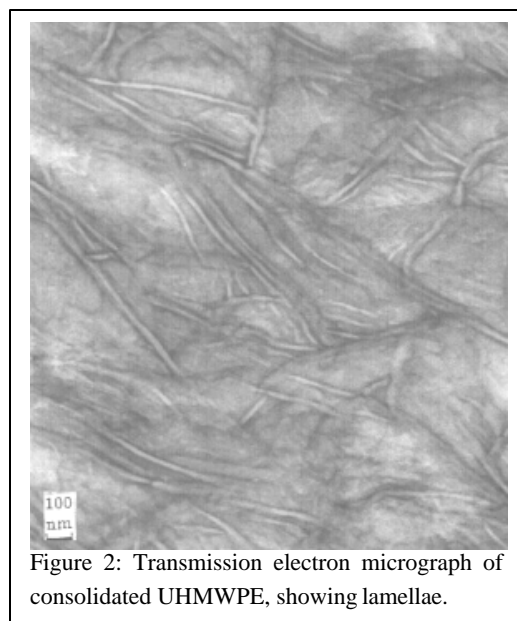
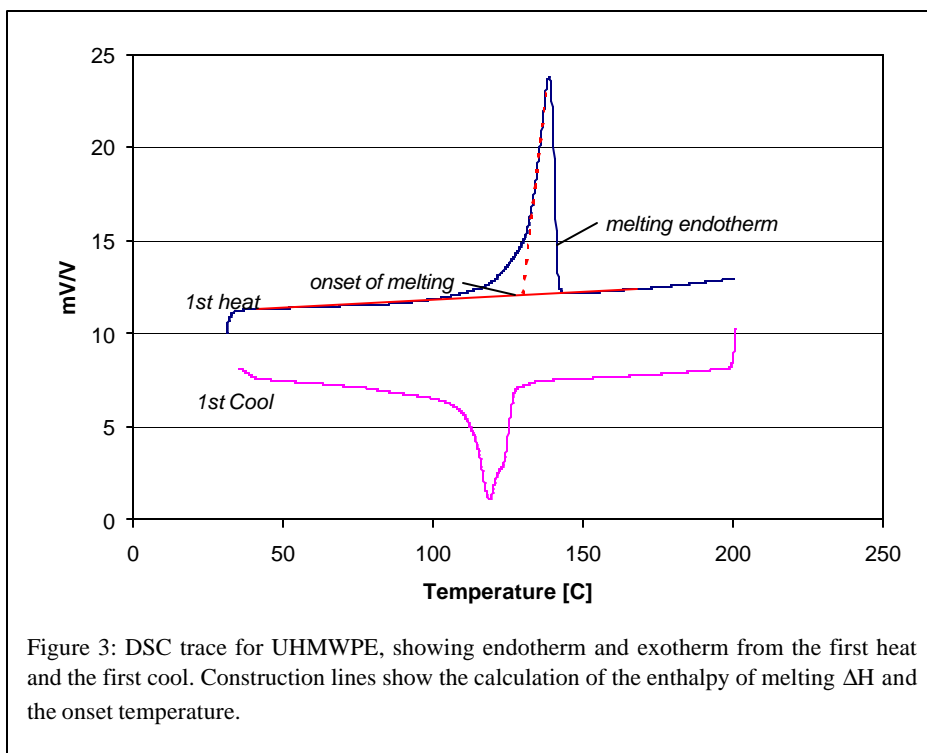


Figure 2: Transmission electron micrograph of consolidated UHMWPE, showing lamellae.

Care must be taken in establishing the construction lines for the crystallinity analysis. Systems with a large distribution of crystal sizes will exhibit a broad endotherm, whence the construction line should begin at very low temperatures (around 25-40°C) in order to capture all the heat absorbed from melting.



Chemical Analysis

When considering the changes in the chemical nature of the UHMWPE with radiation, researchers will usually examine the molecular weight and the *ir* absorbance spectra of the material.

Molecular Weight

Prior to irradiation, the molecular weight and molecular weight distribution is often measured, so that the efficacy of the crosslinking reaction can be calculated *a priori* [3], and changes in distribution due to crosslinking or scissioning can be quantified.

Two techniques are used to examine the molecular weight of UHMWPE, one more commonly than the other. Dilute solution viscometry, the most commonly used technique, will yield the intrinsic viscosity $[\eta]$. In this test, the UHMWPE powder is dissolved in decahydronaphthalene at 140°C, along with a suitable antioxidant, for 1 hour, then transferred via a heated buret into a No. 1 Ubbelohde viscometer held at 135°C. By measuring the elution times of the polymer solution relative to the pure solvent, and knowing the calibration values for the viscometer, the intrinsic viscosity can be calculated.

Through the relationship between the polymer chain size, which is proportional to the molecular weight (assuming no branching), and the polymer-solvent interaction [4], the nominal weight-averaged molecular weight can be estimated as:

$$M_{w,nom} = 5.37 \times 10^4 [\eta]^{1.37}$$

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The other approach, termed gel permeation chromatograph (GPC), allows one to determine the molecular weight distribution, instead of a single statistical moment value. In GPC, the polymer is dissolved in trichlorobenzene at 160°C, and is then forced through a column containing a porous structure which separates the polymer chains according to chain size. A refractometer positioned at the end of the column monitors the concentration of the polymer as a function of time, and therefore chain size. GPC is the only technique that provides the distribution of molecular weights, unless fractionation techniques are employed. The caveat of GPC is that it is often difficult to completely dissolve the UHMWPE. Consequently, the higher molecular weight components are often excluded from the analysis.

Fourier Transform Infra-red Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) has become one of the favored techniques in analyzing the effects of ionizing radiation on UHMWPE. In this test, a broadband infrared source is transmitted through a thin section of UHMWPE (typical thickness 100-200 μm). Chemical species are activated by light at a specific frequency, and will absorb energy at this frequency. A MCT detector on the other side of the specimen monitors absorption as a function of the frequency of the light source. The prevalence of this technique in UHMWPE research arises from two reasons:

1. Many radiolytic products are visible in the *ir* spectrum, and can be quantitatively measured.
2. The interrogation region of the *ir* spectrometer can be focused to a slit size of 10-20 μm . If the user has a manual or motorized stage upon which the sample can be placed, the *ir* spectrum can be mapped as a function of position in the sample.

Because FTIR is a line-of-sight measurement, the absorbance peak heights will depend on the thickness of the specimen. To remove this sample size dependence, researchers will typically normalize the peak height or peak area at the vibration of interest with a reference peak known to be insensitive to the effects of radiation. Common reference peaks used are 1370 cm^{-1} and 2022 cm^{-1} , corresponding to methyl group stretching. It has been found that use of the peak area, rather than peak height, yields more reproducible results.

The ratios of the peak areas at the frequencies of interest to the reference peak are often reported as an *index*. Researchers must be careful to be consistent in the choice of reference peak in order to make quantitative comparisons between their samples and observations made by other researchers, as the absolute value of the index will clearly depend on the reference peak.

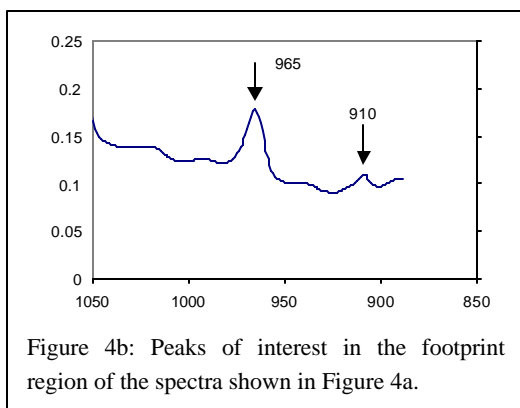
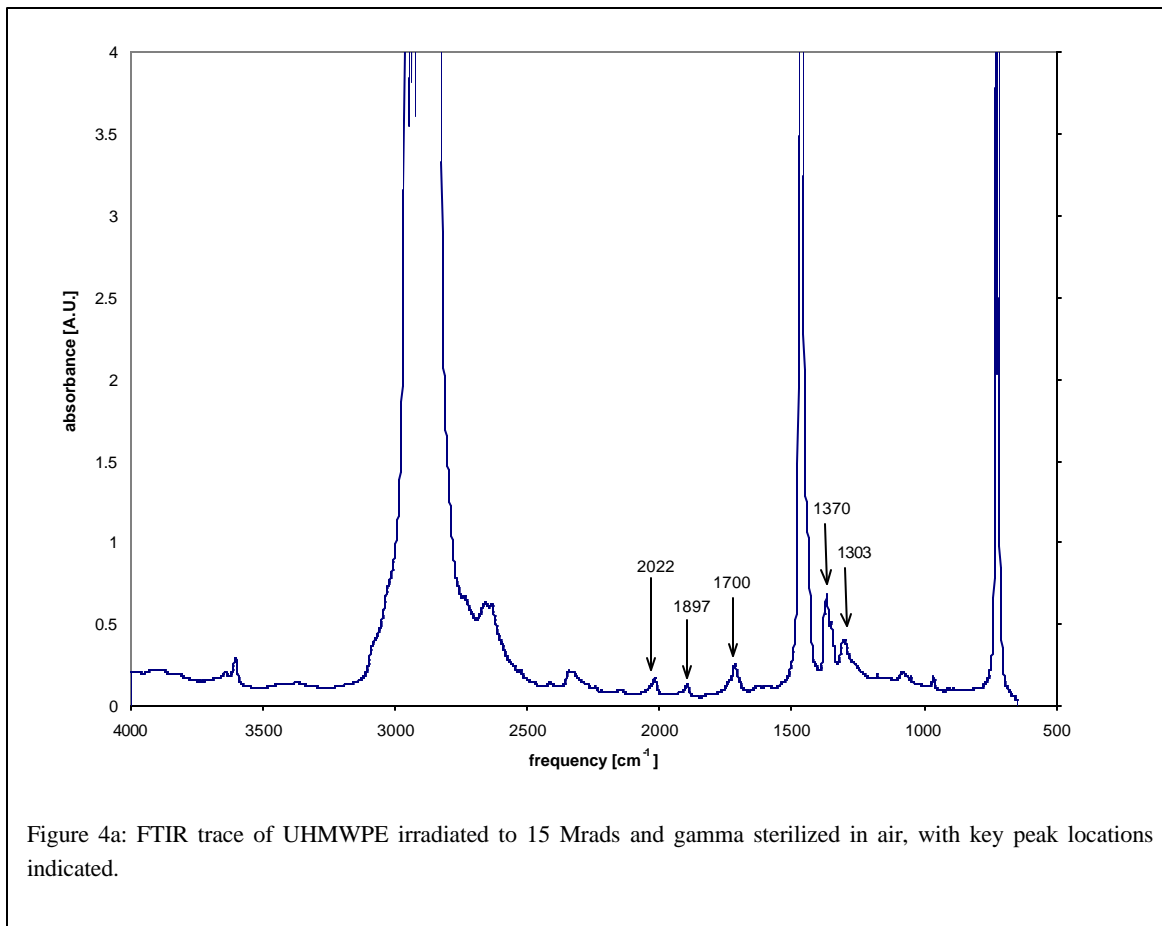
Additional errors are induced when water is present, which appears as noise from 1200-1800 cm^{-1} . Nitrogen purging, or software correction for water, will clean up the spectral signal. Transmission spectroscopy of thin film can often result in Fourier rippling in the footprint region (frequencies less than 1000 cm^{-1}), which can compromise quantitative analysis of peaks in that region. Careful sample preparation can prevent the appearance of the baseline waviness resulting from Fourier rippling.

The key frequencies used to identify radiolytic yields in UHMWPE are shown in Table 2. An example trace of an irradiated UHMWPE is shown in Figure 4.

Table 2: FTIR peak identification

Peak Location [cm^{-1}]	Description
910	Terminal vinyl groups, related to crosslinking and scission
965	Trans vinylene groups, related to crosslinking
1303	Associated with amorphous regions
1897	Associated with crystalline regions

1700	Carbonyl groups, related to oxidation
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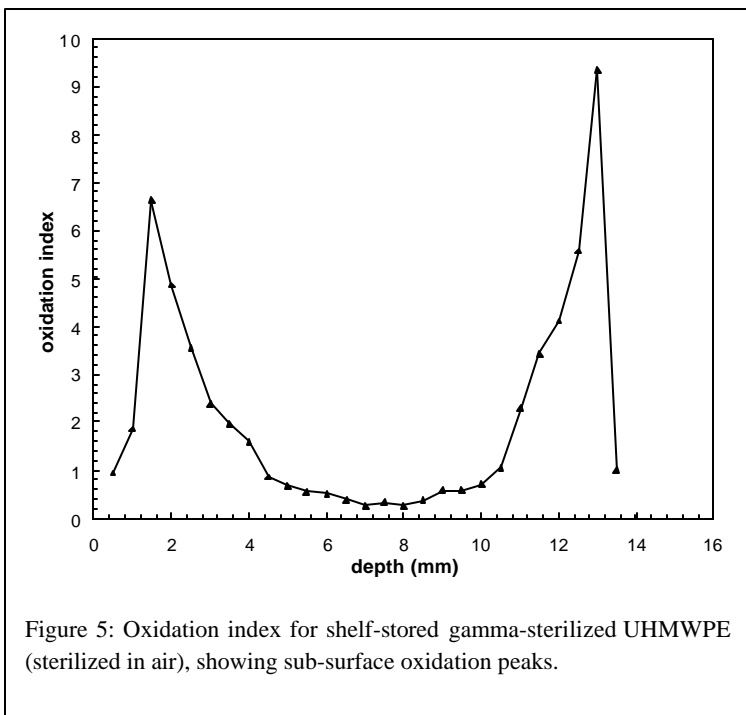


Numerous studies have been conducted to examine the appearance of radiolytic groups found in crosslinked and sterilized UHMWPE tibial inserts and acetabular liners. The most prevalent group examined is the carbonyl group, associated with oxidation [5, 6, 7, 8]. The sub-surface oxidation peak, as shown in Figure 5, has been well-documented by many researchers [9].

The relationship between crosslinking and transvinylene yield has been known for many years, and more recently researchers have been using the approach of using transvinylene measurements as an internal dosimeter for crosslinked UHMWPE [10, 11, 12].

Finally, *ir* spectroscopy has been used to quantify the degree of crystallinity in UHMWPE [13, 14]. Researchers found a linear relationship between the peak at 1897 cm^{-1} and crystallinity determined by X-

ray analysis. However, the results are sensitive to the chemical structure of the polyethylene examined, in particular the presence of chain branching.



Swelling /Sol Gel Analysis

Swelling

Examination of the response of a crosslinked when placed in a good solvent is an effective means of quantifying the crosslinking density. In the current ASTM method (D2765), a crosslinked specimen is weighed, allowed to swell in a chamber containing xylene at 130°C, then re-weighed. The swell ratio q is determined from the weight gain and the densities of the polyethylene and xylene.

While a popular approach, this technique is subject to errors associated with solvent evaporation, uncertainty of steady-state, and the hazards of handling

hot dangerous solvents. Consequently, alternate approaches that avoid removing the sample from the solvent are preferred. In the most popular approach, the change in sample height is monitored with a probe that is in light contact with the sample [3, 15]. An example of the transient response of the swelling of crosslinked UHMWPE is shown in Figure 6. Based on the steady state swell ratio, the interaction parameter χ for polyethylene and xylene at 130°C, and the molar volume of xylene V_1 , the crosslink density ν_x (moles of crosslinks/unit volume) can be calculated from Flory network theory from the following expression:

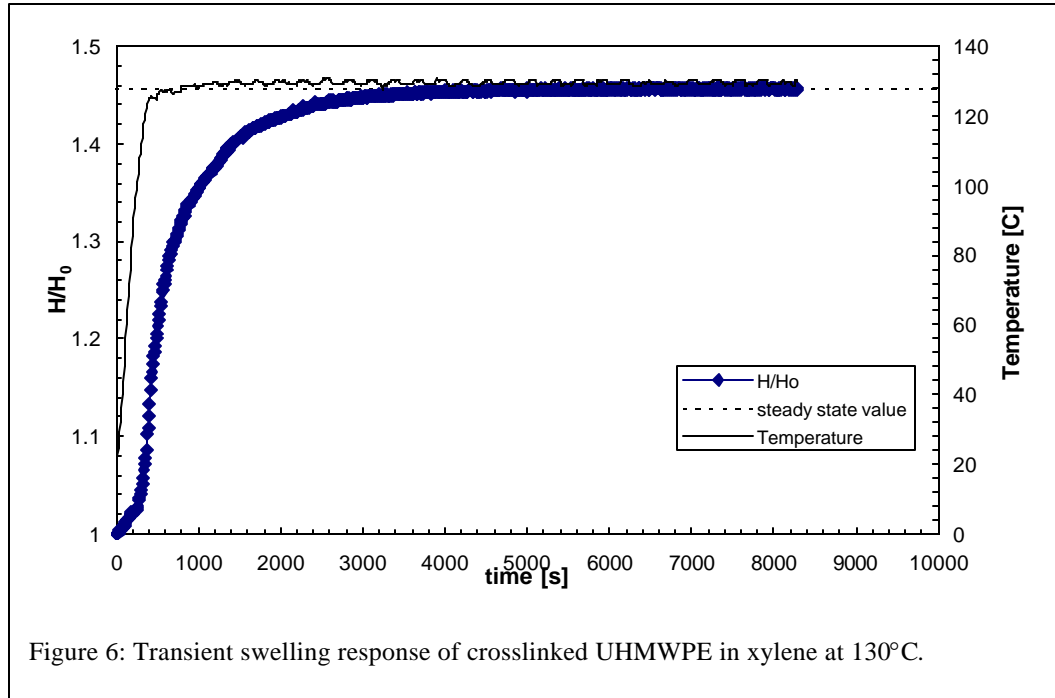
$$\nu_x = -\frac{\ln(1 - q^{-1}) + q^{-1} + c_1 q^{-2}}{V_1 (q^{-1/\beta})}$$

This expression assumes a network with tetrafunctional crosslinking (i.e. no branching).

Sol-Gel Measurements

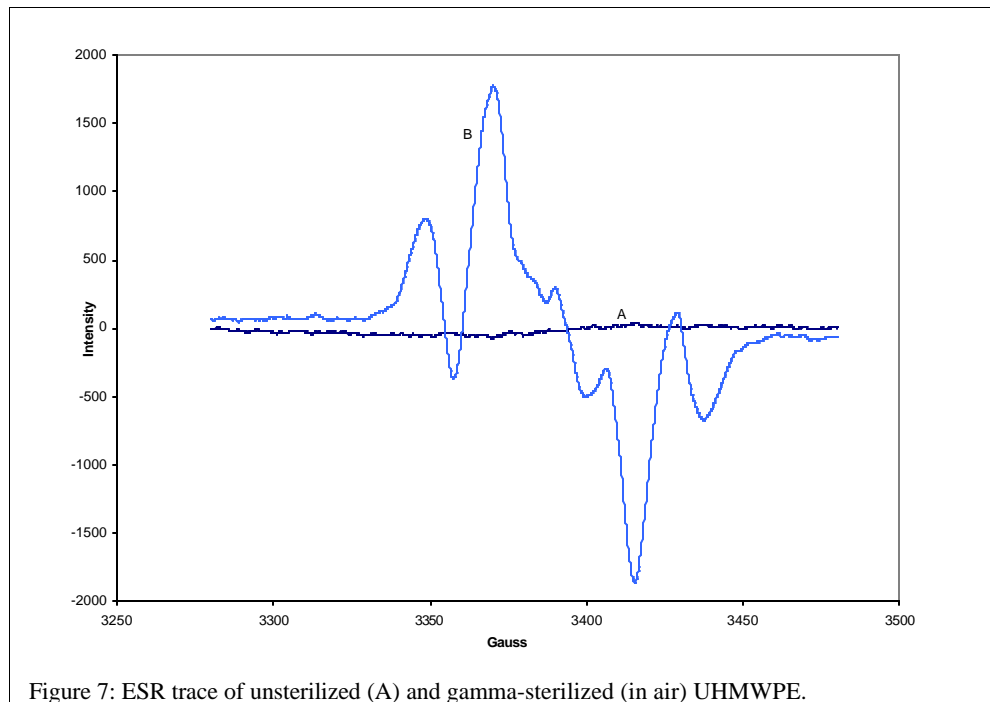
Similar to the current ASTM method for swelling analysis, this test uses weighing methods to determine the degree of crosslinking in polymer systems. However, instead of weighing the solvent uptake in the polymer matrix, one measures the amount of material extracted (i.e. soluble) from the network. In this manner, one measures the percentage of gel, or fully crosslinked, material in the sample. ASTM D2765 describes several methods for making these measurements. In one approach, the sample is carefully weighed, packaged in a pre-weighed porous stainless steel mesh bag, then placed in a flask containing boiling xylene and equipped with a condenser. After 24 hours, the bag and remaining sample are dried in a vacuum oven and re-weighed. This approach can be used effectively for polymer films and unusual shaped

structures. However, it is less effective in computing a crosslink density as the swelling method previously described. Antioxidant must be used in both these methods to prevent thermally-induced chain scission.



Electron Spin Resonance Spectroscopy

Electron spin resonance spectroscopy (ESR) is an effective means of quantifying residual free radicals in irradiated UHMWPE [16]. As free radicals can react with oxygen, forming carbonyls and hence areas susceptible to main chain scission and embrittlement, ESR is sometimes used to anticipate the stability of an irradiated implant to shelf-storage and *in vivo* use. Figure 7 shows typical results.



Trace Element Analysis

Trace element analysis is often performed on the UHMWPE powder prior to consolidation in order to determine the amount of titanium, calcium, chlorine, and aluminum. Mass spectroscopy is usually performed to quantify the yields of these materials, typically reporting results in parts per million. Sample preparation is important in order to get good quantitative results. Samples must be sealed in containers prior to pyrolyzation or microwave digestion of the material; if not, erroneously low concentrations can be measured due to air-borne loss of materials.

Mechanical Analysis

The ASTM has well-described guidelines for performing most mechanical analyses of plastics. This manuscript will not repeat these descriptions, but will rather comment on the techniques, and point out benefits and deficits of the technique.

Compression Testing

Compression testing of UHMWPE is often performed to measure the compression modulus. As irradiation of UHMWPE will change the crystallinity of the matrix, particularly at crosslinking doses in excess of 5 Mrads, the modulus will be affected by radiation. Additionally, researchers can investigate the decrease in modulus with increasing temperature, such as 37°C (body temperature). The modulus is measured from the initial slope of the stress-strain curve, and is thus sensitive to compliance in the compression load frame, transducer resolution, degree of parallelism of the sample surfaces, and slippage between the sample and the machine platens.

Tensile Testing

Tensile testing on dog-bone shaped specimens provides the Young's modulus, yield stress, ultimate tensile strength, and strain to fracture. When testing ductile materials, the researcher must use a strain gauge transducer to monitor strain in the deformation region, rather than rely on crosshead movement, as not all of the deformation is relegated to the necked-down deformation region.

Fatigue Testing/J-Integral

Crack-propagation studies in fatigue are difficult to perform on ductile materials such as UHMWPE. Crack-tip blunting will often affect crack growth and distort the growing crack. Researchers in the metal industry will usually use strain gauges to monitor the crack opening displacement (COD), and use simple geometry to calculate the crack growth. As this approach does not work with ductile materials, most researchers use optical techniques to monitor crack growth.

J-integral tests provide the amount of energy required to initiate crack growth. In order to validate the test, the sample must be in plane-strain conditions, which are independent of sample geometry. With UHMWPE, this condition is very difficult to attain. Consequently, J-integral tests are usually not performed for quantitative studies. For consistent sample sizes, however, the results can be used for relative comparisons. As with fatigue analysis, optical measurements of crack growth are preferred.

Small Punch Analysis

A newer mechanical analysis has emerged in recent years that makes use of the biaxial deformation of small discs of UHMWPE, yielding a stress-strain curve [1]. Researchers have demonstrated a dependence on the area under the stress-strain curve to wear testing, and suggest that the biaxial nature of wearing is the reason for the good comparison [17]. The obvious benefit of this technique is the small sample size, allowing spatial measurement of mechanical properties on retrieved components.

In Vitro Testing

Finally, two standard methods have emerged to anticipate the response of implanted UHMWPE components to *in vivo* use. Accelerated aging, through increased temperatures and oxygen content, is used to try to predict oxidation levels over many years of shelf-storage or *in vivo* conditions [18, 19]. Hip simulators are used to monitor wear behavior under a physiologically-accurate wearing pattern [20, 21, 22]. These two approaches are discussed extensively in other manuscripts.

Conclusions

There is a large battery of tests available to the researcher to examine the effects of radiation on the properties of UHMWPE. These effects include evolution of morphological structure, production of chemical species, and change in mechanical properties. Caution must be used in sample preparation, test conditions, and data interpretation.

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