Ftir and UV-Vis Spectroscopic Investigation of Medical Grade Ultra-High Molecular Weight Polyethylene Blended with the Antioxidant Vitamin-E, Following Simulated Gamma-Sterilization and Shelf-Aged for 10 Years

Trae Lawrence Staggers

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FTIR AND UV-VIS SPECTROSCOPIC INVESTIGATION OF MEDICAL GRADE ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE BLENDED WITH THE ANTIOXIDANT VITAMIN-E, FOLLOWING SIMULATED GAMMA-STERILIZATION AND SHELF-AGED FOR 10 YEARS

by

Trae Staggers

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ABSTRACT

Many medical device applications have begun to incorporate an antioxidant, Vitamin E at low concentrations (0.1 – 0.3 Wt%) within Ultra-High Molecular Weight Polyethylene (UHMWPE) components of total joint replacement. The lowest detectable limit, currently, of vitamin-E within these UHMWPE components, is around 0.3 Wt%, while the most common concentration of vitamin-E in vitamin-E-blended UHMWPE components is 0.1 Wt%. With these components, therefore, science is currently limited to mostly observations of subsequent wear rates of the resulting UHMWPE product and assumptions regarding the effects of vitamin E. To fill this gap, this study has custom-blended a variety of UHMWPE with higher concentrations of vitamin-E (up to 15.0 Wt%) to allow for the direct observation of vitamin E and its antioxidant role within UHMWPE. The samples were treated with ionizing radiation (the subjects of study) as is typically done in the manufacturing process and compared to non-irradiated controls, via Fourier Transform Infra-Red (FTIR) analysis and UV-Vis (Ultra-Violet-Visible spectrum) spectrophotometry, which no study has done before. While such higher concentrations of vitamin-E are not typically used in UHMWPE components of medical devices, they can allow better evaluation of vitamin-E directly, regarding its role in protection from oxidation and resulting degradation. Results suggest anti-oxidant effects at low concentrations of Vitamin-E as expected, but also possible “pro-oxidant” effects of Vitamin E at higher concentrations, and this study provides information which will help medical device manufacturers to improve the successful life of polyethylene components, as well as the community in general to understand the effects of vitamin-E in polyethylene.
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CHAPTER 1

INTRODUCTION

Sterilization of Polyethylene

Several sterilization techniques are used to treat polyethylene, each having its own effect of mechanical properties. Ionizing radiation, such as via gamma radiation, is one sterilization technique. Polyethylene undergoes gamma sterilization while exposed to air/oxygen, the ionizing radiation breaks molecular bonds, forming free radicals; this can result in oxidation and embrittlement of Polyethylene. Other sterilization techniques include the use of substances such as gas plasma and oxides without use of ionizing radiation, which can avoid free radical formation. A study was done to using acetabular cups for total hip arthroplasty, in a hip joint wear simulator to test the percentage of mass loss of UHMWPE vs. highly crosslinked UHMWPE (HXPE) and HXPE containing Vitamin-E (HXPE-VE) showing that the HXPE-VE had the highest wear rate of 225% after a two million cycles following simulated aging (Taddei et al., 2017). This could be due to the fact that there was a very low dosage of vitamin-E incorporated into the Polyethylene. In addition to this, the elevated temperature further decreased the wear of the material, maximized vitamin-E grafting, and increased the cross-linking of the UHMWPE (Oral et al, 2012). In opposite, second generation sterilization of Highly Cross-Linked Polyethylene use gas plasmas and oxides for sterilization to avoid further free radical production. Companies such as Zimmer-Biomet, Smith & Nephew, Marathon (Depuy Synthes), Teijin Nakashima Medical, and ECiMa (Corin) have used Ethylene Oxide (EtO) for sterilization (Yamamoto et al, 2017). In addition, there is a rather different form of
sterilization which uses low atmospheric-pressure plasma for anti-microbial decontamination. Different environments may affect the outcome of the polyethylene due to vitamin-E. One study used real-time aging environments over three years in three different cases. The first case was a room temperature environment, the second case was in air at 40°C, and the third case is a submersion in an aqueous environment at 40 degrees Celsius, but also dissolved in an oxygen concentration similar to synovial fluid. The specific material used was GUR1050 UHMWPE (30 x30x10 mm specimens). They were gamma-irradiated to 85-kGy in an inert gas and involved vitamin-E doping (soaking in hot Vitamin-E) at 120°C for 5 hours. It was also homogenized in argon for 64 hours (Rowell et al., 2009). A study compared UHMWPE that was sterilized by gamma irradiation in air vs. gamma irradiation in Ar gas vs. sterilized via ethylene oxide, vs. unsterilized, showing that oxidation was highest at the specimen surface for that which was gamma irradiated in air and lower for ultrahigh molecular weight polyethylene gamma irradiated in Ar gas. Unsterilized UHMWPE and EtO sterilized UHMWPE have been observed to not undergo oxidation (Ries et al., 1996), and another study used backscattered electrons to increase crystallinity in UHMWPE after gamma irradiation when in contact with a stainless-steel backing. As crystallization forms, the mechanical properties of the polymer changes (Barron et al., 2015).

**Significance of Vitamin-E in Polyethylene**

Polyethylene components of implants, such as hip implants and knee implants, as susceptible to oxidation, primarily due to effects of ionizing radiation exposure as discussed in the preceding sections. Oxidation leads to degradation of the polyethylene material. Still what leads to oxidation is free-radicals, which result from the broken molecular bonds within the polyethylene when exposed to ionizing radiation; these free radicals then react with oxygen molecules (such as are present in air, and within a human body). This in turn reduces the
mechanical properties and causes wear of the material. Antioxidants prevent these interactions between free radical and oxygen; there are many examples of this application there are very many examples of this application with many materials, and even is the case within the human body itself (for example, antioxidants within some foods have this same protective effect). Some antioxidants are not for human use but are appropriate for industrial applications like preservation of rubber products or paint. Some antioxidants are more appropriate for the human body, and are considered biocompatible; one popular example of such an antioxidant is vitamin-C. What this line of discussion is leading to, of course, is the use of antioxidants in medical-grade UHMWPE, which requires that it has to be added to the UHMWPE somehow. Some additives/antioxidants don’t work well with UHMWPE. Vitamin-C, for example, does not blend well with UHMWPE and cannot withstand the temperatures used in the manufacturing process. Vitamin-E, on the other hand, does blend well with UHMWPE (and can also be diffused into UHMWPE via heat), and incorporates within the material appropriately. The vitamin-E is then present to react with free radicals before oxygen does, therefore preventing oxidation from occurring. So, without the use of vitamin-E, the polyethylene material is more vulnerable to oxidation after radiation exposure, such from crosslinking or gamma irradiation (crosslinking is discussed more specifically in Section 1.3). Studies have supported this concept that vitamin-E prevents oxidation, and ultimately, wear, by showing reduced wear rate in UHMWPE that has been blended with vitamin-E (Feskanin et al., 2019). There are other methods of free radical elimination after crosslinking in UHMWPE in, such as by heating at or just below the melt temperature just after radiation-crosslinking, but reduce the mechanical properties of the material, may not eliminate the free radicals as efficiently, and do nothing for subsequent radiation exposure such as gamma-irradiation. Because of the addition of vitamin-E in the
HXPE, there is a little to no need of post irradiation techniques, such as annealing or melting of the material.

**Effects of Vitamin-E in Polyethylene**

As mentioned before, vitamin-E is present for the induction of oxidative stability and improvement of mechanical properties after or during irradiation. Many studies have shown positive effects of vitamin-E when blended/grafted with UHMWPE. One study done at Zimmer Biomet (Zimmer et al, 2014) used Vivacit-E HXPE, which is grafted vitamin-E onto HXPE during Vivo oxidation for total knee arthroplasty. After 33 weeks of accelerated aging, the HXPE maintained the same mechanical properties from the initial stage of aging to its final stage. According to the article, it showed a 94% wear reduction compared to conventional Polyethylene. In addition, it showed a comparable wear to Longevity HXPE after 75 million cycles. It also showed a high resistance to delamination and further strengthened the material. This article found that through extraction testing, there was no extraction of the vitamin-E out of the material after using polar and non-polar solvents. Overall, this study has found lower wear rates, induced oxidative stability, reduced lipid absorption, and increased strengthening of the material. In addition to this, vitamin-E containing polyethylene is a good substitution in terms of reduced abrasive residue powder formation inside of the hip and knee joint as compared to traditional metals (Matsumoto et al, 2018). When tested for compression and tension testing, UHMWPE and vitamin-E-containing Polyethylene (VEPE) had a higher young’s modulus as compared to HXPE, resulting in greater compressive strength. The average Young’s modulus for each polymer was 748.2 (SD 34.7) MPa for UHMWPE, 636.2 (SD 12.0) MPa for the 75-kGy HXLPE and 803.3 (SD 12.0) MPa for VEPE respectively. In addition, the elastic modulus for tensile testing for HXPE was lower than that of the UHMWPE and VEPE that resulted in a
difference of around 21.4% and 40% (p< 0.05) (Lu et al, 2018). As can be seen, many studies only show the correlation of vitamin-E dosage and the amount of oxidation due to the concentration of Vitamin-E, but no study has been shown to thoroughly study what happens to the molecular structure of the material when vitamin-E is present over an extended period of time, with the exception of one study. This study detected the presence of primary, secondary, and tertiary nitrates after oxidation has occurred over a period. The wavelength ranged from 2100 to 1550 cm$^{-1}$. The study has shown that there was a presence of primary nitrates at 1642 cm$^{-1}$, along with secondary nitrates at 1631 cm$^{-1}$, and tertiary nitrates at 1629 cm$^{-1}$ (Bracco et al., 2006). However, this study was not done with the presence of Vitamin-E. This sparks the idea to further study the effects of vitamin-E on the molecular level. The purpose of this research is to extensively study the changing of the molecular bonds of the UHMWPE based on the concentration of vitamin-E as light is transmitted or absorbed at different wavelengths.

**Applications of Vitamin-E**

The term “crosslinking” has been referred to several times in the preceding sections. Polyethylene molecules can be envisioned as strands of spaghetti; UHMWPE molecules can be envisioned as very long strands of spaghetti. Before crosslinking these strands can be envisioned as “wet” and able to move relative to one another, but are fairly well intertwined, so still hold together pretty well. Crosslinked polyethylene is more like dry/sticky spaghetti noodles; this is because the crosslinking is performed via ionizing radiation (such as gamma radiation), which creates the aforementioned free radicals; these free radicals react with each other, and “stick” the polyethylene molecules together, forming “crosslinks” and strengthening the material. Many unpaired electrons remain, however, with are susceptible to oxidation. So, it is around this point of the manufacturing process (i.e., the crosslinking treatment) that vitamin-E needs to be present.
UHMWPE first exists in a powder (“resin”) form; this powder is then formed into a solid by pressure and heat, referred to here as “consolidation.” There are two primary methods for incorporation of vitamin-E into the UHMWPE: (1) Blend the vitamin-E with UHMPWE powder resin before consolidation, then consolidate the vitamin-E/UHMPWE blend, then crosslink the solid material, for which the vitamin-E is already present to react with the resulting free radicals (Wernle et al, 2016). The other method (2) is for the Vitamin-E to be applied after consolidation and crosslinking; this is done by soaking the solid, already-crosslinked (and therefore, already free-radical-containing) UHMWPE in a hot fluid of vitamin-E, therefore diffusing the vitamin-E the vitamin-E at a temperature that is just below the melting point of UHMWPE; the UHMWPE is then removed from the vitamin-E and heated further to distribute the vitamin-E throughout the thickness of the UHMWPE components (known as “homogenization”). These two methods are referred to as “blending” and “diffusion” of vitamin-E into UHMWPE. One advantage of blending is that the vitamin-E is already present before radiation exposure; a disadvantage is it reduces crosslinking by reacting with the free radicals before they can form crosslinks (Popoola et al., 2015), so some experimentation is necessary to determine the appropriate radiation dose to achieve the desired level of crosslinking (which is more well-known for UHMWPE without vitamin-E); another important feature is the bonding of the polymer chain to the aliphatic tail of the vitamin-E molecule, as shown in Figure 5 (Oral et al., 2012).

Figure 1: Representation of Vitamin-E Molecule
An advantage of diffusion is that it is easier to achieve the desired crosslinking, as the vitamin-E is not present during that step; one disadvantage is that more free radicals do form initially (from the radiation during crosslinking), and the heat that is necessary for diffusion and homogenization is similar to annealing of the material. Still, with either method (blending or diffusion), vitamin-E is incorporated into the UHMPWE for subsequent protection; neither is clearly superior to the other; both are good and serve their purpose of preventing oxidation adequately.
Experimental Techniques for Tracking Vitamin-E in Polyethylene

There are various techniques that scientists have used throughout the years in order to study the effects of the molecular changes of Polyethylene, due to vitamin-E blending/grafting. The techniques for this research topic, such as UV/Vis Spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR), will be closely examined for the molecular changes of an aged material (at least ten years of age), that is blended/grafted with vitamin-E at a time $t = 0$.

UV/Vis Spectrophotometry is a used such that a very thin sample is placed in a sample holder that has a small slit. This slit allows light to be transmitted through the material to test for percent transmission and percent absorption as well as various other measurements. During this instrumentation, a graph with variables such as intensity or absorbance will be plotted versus a wavelength spectrum. The wavelength spectrum typically ranges from 200 nm to 800 nm. The spectrum is also broken up into two regions: Ultra-Violet region (200 - 400 nm) and the Visible region (400 – 800 nm). The Ultra-Violet region has a shorter wavelength and a higher frequency than that of visible light and infrared light. There are certain shifts in wavelength that can occur in a measurement such as a red shift or blue shift. The Bathochromic Shift (red shift) occurs when a maximum from absorption shifts toward longer wavelength, due to a substance that alters the intensity or the wavelength of the absorption of the material, typically a liquid. The Hypsochromic Shift (blue shift) is the opposite of a red shift in the fact that the absorption maximum shifts to a shorter wavelength, due to changing the solvent altering the conjugation of the material (also typically a liquid). When dealing with UV/Visible Spectroscopy, there is a
restriction to certain regions or functional groups in organic compounds. These compounds contain valence electrons (\(\pi\), \(\sigma\), and \(n\) electrons) that have a required excitation energy that is usually low. These absorptions take place in one of three transitions known as \(\sigma \rightarrow \sigma^*\), \(n \rightarrow \sigma^*\), and \(n \rightarrow \pi^*\). The \(\sigma \rightarrow \sigma^*\) transition requires a very large energy to become excited and its absorbance is typically under 200 nm, so it is not visible to the human eye. The \(n \rightarrow \sigma^*\) transition consists of atoms with lone pairs of electrons and need little energy. They initiate when light of a wavelength of 150 – 250 nm is introduced. This transition occurs the least in organic compounds. The \(n \rightarrow \pi^*\) transition falls between 200 and 700 nm and must consist of an unsaturated group for the existence of pi electrons. Most organic compounds fall under this transition for absorption. Here, it is important to note the various wavelengths in which vitamin-E Indices may be measured. One study found the occurrence of Vitamin-E ranging from a wavelength of 250 nm up to 320 nm with a decrease in Vitamin-E Concentration as the irradiation increased. (Rowell, S). it is desired to find out whether these results will similarly match their findings.

Fourier transform Infrared Spectroscopy is a technique that is used to determine specific functional groups. It generally starts as an interferogram, which is a signal of a complex manner that includes all the frequencies of the infrared spectrum. The mathematical phenomena of the Fourier transform is capable of taking all frequencies from the interferogram and reproduce them identically through a spectrometer known as the Fourier Transform Infrared Spectrometer. During the process, a material either absorbs or transmits infrared light on the visible light spectrum. This causes vibrations on a molecular scale. Molecular changes can occur as a stretching, compressing, or bending order. Similar to UV/Vis Spectroscopy, FTIR can also measure percent transmittance and percent absorption, which both have an inverse relationship with each other. This technique was used to measure the molecular changes in the Polyethylene...
over a span of at least ten years. However, FTIR measures in the units of wavenumber (cm^-1), while UV/Vis Spectroscopy measures in wavelength with a unit of nm. During FTIR measurement, as the wavelength increases, the frequency decreases as given by the energy formula, \( E = \frac{hc}{\lambda} \), where \( h \) represents Planck’s constant, \( c \) represents the speed of light, and \( \lambda \) represents the wavelength. The energy of a photon is equally proportional to the frequency as \( f = \frac{hc}{\lambda} \). The FTIR curve spectrum can be divided into two regions. The region ranging from around 1500 cm^-1 and lower can be identified as the fingerprint region. This region has a series of complex molecules due to a large amount of absorption taking place. The remaining region ranging above 1500 cm^-1 can be identified as the functional group region. Both regions have a series of signals or peaks that can occur in a broad or sharp shape. Along with the shape of the peak, a particular intensity is associated with each of them. The intensity of a signal increases when there is a high absorbance and low transmittance.

In order to find the molecular composition of a material, it must be known what each curve represents. The shape of the curve is very important when identifying a certain functional group. If the peak is very broad, then functional group is a polar bond, such as hydrogen bonds, carbonyl bonds, etc. This results from many intermolecular bonds that occur within the molecule.
For example, this table from an article by Joseph Koo illustrates various types of Hydrogen bonding (Koo et al., 2002). As can be seen, there are many intramolecular bonding that occurs in each of these molecules, which would result in a broad peak in a wavenumber vs. absorbance Curve. There are a few common compounds that can be measured using this technique, such as the Carbon – Oxygen compound (1630 – 1850 cm\(^{-1}\)) , the Carbon – Carbon compound (1620 – 1680 cm\(^{-1}\)), the Oxygen – Hydrogen compound (3200 – 3650 cm\(^{-1}\)), and the Nitrogen Hydrogen compound (3300 – 3500 cm\(^{-1}\)). There are various other molecular compositions that can be identified from the FTIR technique. For example, FTIR can show the presence of aldehydes and ketone groups. An aldehyde consists of a carbonyl group and a hydrogen attached to it an aldehyde can be measured around 1700 cm\(^{-1}\) due to its carbonyl
bond. It also consists of a Carbon-Hydrogen bond that can be seen around 1370 \( cm^{-1} \), which is just to the side of the alkane region (approximately 2900 \( cm^{-1} \)). A Ketone has a carbonyl group with two hydrogens attached and it can also be measured around 1700 \( cm^{-1} \). However, the ketone group does not consist of Carbon-Hydrogen groups, so it will not show a peak next to the alkane group. Other groups such as Ether and Ether, Amines and Amides, etc. can also be measured.

![Figure 3: Example Spectrum for FTIR Measurement:](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3986646/)

In order to measure the oxidation index (OI), which estimates oxidation damage, the area under the C=O peak at approximately 1715 \( cm^{-1} \) is divided by the area under the standard peak at 1370 \( cm^{-1} \). The trans-vinylene index (VI), which estimates the radiation dose, the area under the C = C band at 965 \( cm^{-1} \) is divided by the area under the Standard peak at 1370\( cm^{-1} \). In addition, the crystallinity index (CI), which estimates the amount of crystalline region, can also be measured by dividing the area under the Crystalline peak at 1900 \( cm^{-1} \) (a.k.a. the
polyethylene skeletal absorbance peak) by the area under the Amorphous peak at $1300\,cm^{-1}$. A peak at 1262 (not in this image) can be used to estimate vitamin-E content.

For these two techniques, the scan rate is very important for getting accurate results. The scan rate is a technique that specifies how fast the operation is done. Slowing the scan rate signifies a greater focus of light going through the material, which in turn gives finer details on the absorption and transmittance of light in the material. Both techniques have two modes of measurement: Reflection mode and transmission mode. Reflection mode is used for measurement when the sample is opaque; little to no light is transmitted through. Transmission mode is used to measure a sample that is transparent, which allows light to transmit through the material.

**Experimental Methods:**

To conduct this experiment, a wide range of materials with different Vitamin-E concentrations were tested. These materials were aged by a span of over ten years. The concentrations ranged from 0% Vitamin-E up to 15% Vitamin-E, all with similar aging. Each of these different materials had both a control, which means that they are not irradiated. In addition, each material had an irradiated sample. The irradiated samples underwent gamma irradiation in an environment with nitrogen gas. Below are the specific samples that underwent the experimental techniques:
Samples Ranging from 0% to 15% Vitamin-E Concentration

Figure 4: Samples for 0% Control (non-irradiated) (left) and 0% V.E. irradiated at 50 KGY in Air (right)

Figure 5: Samples for 0% V.E. Irradiated at 100 KGY (left) and 0.5% V.E. Control and Nitrogen Gamma irradiated (right)
As can be seen optically, the color intensity seems to increase almost proportionally with the concentration of vitamin-E in each Material, with the 15% vitamin-E blended sample having the darkest color. These samples were tested using all the different experimental techniques to be tested for similarities in data. For the FTIR, three samples of each vitamin-E dosage were cut in
very thin slices, preferably with the same thickness. Each of the three samples from that bulk material was tested in three regions: Top, middle, and Bottom. At the end of the testing of that one Vitamin-E concentration, there would be a total of nine measurements. This was done to specify whether there were any major differences in the molecular composition and deviated thickness in different areas of these thin samples. This step was completed for both the control sample and the gamma irradiated sample for each concentration of vitamin-E. Each of the three samples was then placed into a separate tray that would then get placed underneath a laser for measurement. This technique was completed in transmission mode. Data was extracted by taking the area underneath the curve at different wavelengths to signify the density of various molecular bonds. To minimize the amount of error in data, averages were taken from the three samples if each dose and plotted as one data point. For instance, the top, middle, and bottom region of each of the three samples were all averaged together and plotted as one data point. This will take the thickness into account, considering that it is highly difficult to precisely cut each sample with the same thickness. To determine the OI more specifically, the areas under these peaks are measured via integration of the signal using the software associated with FTIR instrument; this software was called OMNIC™ Picta; a screenshot is shown in Figure 4. The experimental procedure to conduct measurements for FTIR is as below.
The polyethylene samples were placed across the three holes shown (as Sample 1, Sample 2, and Sample 3); each sample was tested at three locations, called Top, Middle, and Bottom which corresponded to the upper region of the sample (closest to the “top” of the hole), the middle of the sample, and the bottom (closest to the “bottom” of the hole).

The whole objective was to observe a trend of the molecular shifts of the material over time. Likewise, the same samples were used in the UV/Vis Spectrophotometry measurements. Unlike FTIR, UV/Vis Spectrophotometry cannot measure different regions of a specific material in great detail. To compromise, each of the three samples was tested once for measurement. As a result, instead of nine total measurements, each concentration only had three total measurements. The three samples were then averaged into one data point. Similarly, in transmission mode, the materials were tested and observed for any unusual pattern that may have taken place to be studied further.
The UV/Visible Spectrometer is used in a similar manner. The same samples that were prepared to the FTIR techniques will be used for the UV/Visibly Spectrophotometry measurements. The UV-Visible Spectrophotometry measurements were measured using the Thermo-Scientific Evolution Spectrophotometer as below:

![Thermo-Scientific Spectrophotometer](https://www.azom.com/equipment-details.aspx?EquipID=7215

The samples are cleaned with 90% Isopropyl alcohol and placed in a sample holder that has very small slits in them. The sample sizes are relatively small and it is important to make sure that the sample holder that is used, has a slit that is smaller than the sample itself so that no free space will allow light to pass through without going through the sample first. The sample is then placed inside of the Spectrophotometer for measurement. Inside were two pins to hold the sample holder in place in from of a laser. The sample holder is properly placed in front of the laser such that the laser beam shines through the sample and the transmitted light is detected by a detector directly across from the laser. There are three of each sample, so each concentration of Vitamin-E (both irradiated and non-irradiated) were tested, which resulted in three total
measurement for each control and Nitrogen Gamma Irradiated sample for each concentration of vitamin-E.
CHAPTER 3

EXPERIMENTAL RESULTS

Experimental Results for FTIR:

The data shown below represents the absorbance vs wavelength measurements of the UHMWPE at the varied dosages. (Due to conflicts of covid-19, plots for 0% Control/irradiated as well as 10% Control/irradiated are not displayed.)

Figure 10: FTIR Tested 0.5% V.E Sample 1 Control Bottom(left), Middle(middle), & Top(right)

Figure 11: FTIR Tested 0.5% V.E Sample 2 Control Bottom(left), Middle(middle), & Top(right)
Figure 12: FTIR Tested 0.5% V.E Sample 3 Control Bottom(left), Middle(middle), & Top(right)

Figure 13: FTIR Tested 0.5% V.E Sample 1 Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)

Figure 14: FTIR Tested 0.5% V.E Sample 2 Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)
Figure 15: FTIR Tested 0.5% V.E Sample Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)

Figure 16: FTIR Tested 1% V.E Sample 1 Control Bottom(left), Middle(middle), & Top(right)

Figure 17: FTIR Tested 1% V.E Sample 2 Control Bottom(left), Middle(middle), & Top(right)
Figure 18: FTIR Tested 1% V.E Sample 3 Control Bottom(left), Middle(middle), & Top(right)

Figure 19: FTIR Tested 1% V.E Sample 1 Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)

Figure 20: FTIR Tested 1% V.E Sample 2 Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)
Figure 21: FTIR Tested 1% V.E Sample 3 Nitrogen Gamma Bottom(left), Middle(middle), & Top(right)

Figure 22: FTIR Tested 15% V.E Sample 1 Control Bottom(left), Middle(middle), & Top(right)

Figure 23: FTIR Tested 15% V.E Sample 2 Control Bottom(left), Middle(middle), & Top(right)
Figure 24: FTIR Tested 15% V.E Sample 3 Control Bottom (left), Middle (middle), & Top (right)

Figure 25: FTIR Tested 15% V.E Sample 1 Nitrogen Gamma Bottom (left), Middle (middle), & Top (right)

Figure 26: FTIR Tested 15% V.E Sample 2 Nitrogen Gamma Bottom (left), Middle (middle), & Top (right)
The graphs above represent the raw data of each individual sample from 0.5% to 15% vitamin-E For Non-Irradiated and Gamma-Irradiated Polyethylene. The next figures below will be superimposed graphs of each individual sample (Top Region, Middle Region, Bottom Region) to better understand the relationships of each.
Figure 28: FTIR Spectrum of 0% Vitamin-E Control (non-irradiated), sample 1, Top/Middle/Bottom regions

Figure 29: FTIR Spectrum of 0% Vitamin-E Control (non-irradiated) Sample 2, Top/Middle/Bottom regions
In the first sample of 0% vitamin-E UHMWPE(sample 28), it is observed that the TOP location had undergone slightly higher oxidation than the Middle and Bottom, as can be seen by the larger peak around 1720 cm$^{-1}$, which the normalization peak at 1370 cm$^{-1}$ is the same for all. If the peak at 1370 cm$^{-1}$ would have been larger for the Top location, then the oxidation measurement (Oxidation Index (OI)) would have been lower, as OI is determined by the ration of the 1720 cm$^{-1}$ peak to the 1370 cm$^{-1}$ peak.

*Figure 30: FTIR Spectrum of 0% Vitamin-E Control (non-irradiated) Sample 3, Top/Middle/Bottom regions*
In the second sample (Figure 29), all locations had about the same measurements; however, it is hard to tell visually if the area under the normalization peaks (at 1370 cm\(^{-1}\)) are significantly different.

The third sample (Figure 30), the FTIR spectra were all nearly identical, more so than Samples 1 and 2. Overall, even though one location of Sample 1 had slightly larger oxidation peak than the others, all of the samples of 0% vitamin-E can be said to have been about the same. This is, of course, as expected, as they were all of the same sample type, but is a good check to confirm there are not unexpected variations within samples, locations within each sample, or variations that could be due to other factors such as the testing procedure itself.

![Graph showing FTIR spectra comparison](image)

Figure 31: Example Comparison for 0% Vitamin-E Samples 1, 2, and 3
Finally, in Figure 31, all locations of all three samples can be compared. The FTIR spectra of Samples 1, 2, and 3 (Red, Green, and Blue, respectively) are seen to be a little different for each sample around the oxidation peak of 1720 cm\(^{-1}\); however, their normalization peaks at 1370 cm\(^{-1}\) change proportionally. So, the ratios of the two peaks are about the same for each, which are more specifically confirmed via measurements of the areas under the peaks. The primary factor which makes the peaks larger is the thickness of the sample; while care was taken to make all of the samples equal thickness, it is unavoidable to make them exactly the same thickness, which is normal. This is the advantage of the normalization peak, as it compensates for these small differences in sample thickness.

![Wavenumber Vs. Absorbance](image)

*Figure 32: Comparison of 0.5% Vitamin-E Control Sample 1, Top, Middle, and Bottom*
Figure 33: Comparison of Control 0.5% Vitamin-E Sample 3, Top, Middle, and Bottom
Figure 34: Comparison of Control 0.5% Vitamin-E Sample 3 Top, Middle, and Bottom

As for samples 1 and 2 of the control for 0.5% vitamin-E, the bottom and middle regions have similar oxidation peaks and as well as normalization curves around 1370 cm\(^{-1}\). The top region is slightly lower than the bottom and middle region. The middle region in sample 1 has the highest oxidation index. However, since each peak lowered by similar proportions, the oxidation index would be unaffected.

Sample three has similar peaks at each region leaving the oxidation index (1715 cm\(^{-1}\)) and trans vinylene (965 cm\(^{-1}\)) yielding similar results with a trans vinylene measurement close to zero. Even though all peaks look similar, the bottom region of sample 3 has a higher oxidation index at 1.18.
Figure 35: Comparison of Irradiated 0.5% Vitamin-E Sample 1 Top, Middle, and Bottom

Figure 36: Comparison for 0.5% Irradiated Vitamin-E Sample 2 Top, Middle, and Bottom
Figure 37: Comparison for 0.5% Irradiated Vitamin-E Sample 3 Top, Middle, and Bottom

The peaks for 0.5% Nitrogen Gamma differed a bit more than that of the control. Sample 1 had similar peaks in the bottom and middle region, but not at the top region. The top region has a higher trans vinylene measurement along with the highest oxidation index.

The peaks in sample two were displaced with close to equal spacing with the bottom region having the highest oxidation index and the top region having the highest oxidation index and transvinylene measurements.

Sample three had slightly similar peaks in the bottom and middle region with the top region when compared to the top region. The top region yielded the lowest trans vinylene and oxidation index while the bottom region resulted in the highest trans vinylene and oxidation index.
Figure 38: Comparison for 1% Control Vitamin-E Sample 1 Top, Middle, and Bottom

Figure 39: Comparison for 1% Control Vitamin-E Sample 2 Top, Middle, and Bottom
In the plots for 1% vitamin-E Control, each sample had distinct similarities for each of the carbonyl, carbon-hydrogen, and Trans Vinylene peaks. Sample 1 had similar trans vinylene and oxidation index measurements with a trans vinylene measurements of approximately zero.

Sample 2 also has trans vinylene measurements of zero for the top, middle and bottom regions. The oxidation index for the to region is slightly higher than that of the middle and bottom region by approximately .002.

Sample 3 seems as if the peaks for the Trans Vinylene is approximately zero for all three regions. All three samples have similar oxidation indexes with the top region being slightly larger by .001.
Figure 41: Comparison for 1% Irradiated Vitamin-E Sample 1 Top, Middle, and Bottom

Figure 42: Comparison for 1% Irradiated Vitamin-E Sample 2 Top, Middle, and Bottom
As seen from the figures above, sample 1 has a higher oxidation index in the top region whereas the bottom region has a higher trans vinylene measurement. Similar to sample 1, sample 2 has a higher oxidation index in the top region with the bottom region having the highest trans vinylene measurement. However, there is no big difference within these measurements with a deviation of about .005.

Sample 3 has similar trans vinylene measurements and oxidation indices in the top and middle region with a small but negligible difference of about 0.02 in the bottom region.
Figure 44: Comparison for 15% Control Vitamin-E Sample 1 Top, Middle, and Bottom

Figure 45: Comparison for 15% control Vitamin-E Sample 2 Top, Middle, and Bottom
The 15% vitamin-E Control for sample 1 showed similar peaks in the middle and top region, leaving a deviation in the bottom region. Samples 1 and 2 had slightly higher oxidation indices and trans vinylene measurements than the bottom region.

Sample 2 resulted in similar oxidation peaks and trans vinylene peaks. Sample 3 shows higher peaks in the middle and top region with lower peaks in the bottom region, which has the lowest oxidation index and Trans Vinylene.

Sample 3 shows similarities in bottom and middle regions yielding sample 3 to have a lower trans vinylene measurement. All three regions have similar oxidation indices.
Figure 47: Comparison for 15% Irradiated Vitamin-E Sample 1 Top, Middle, and Bottom

Figure 48: Comparison for 15% Irradiated Vitamin-E Sample 2 Top, Middle, and Bottom
Sample 1 in 15% Vitamin-E Control shows similar peaks for oxidation and transvinylene for the middle and bottom region. The top region shows the lowest oxidative index and transvinylene measurement. The middle region shows the highest oxidation index along with the highest transvinylene measurement.

Samples 2 has peaks that are similar to sample 1. The top region in sample 2 has the highest oxidation transvinylene by a difference of 0.3 compared to the bottom and middle region.

In sample 3, the peaks shown are more widely spread in terms of intensity compared to samples 1 and 2. Similar to sample 2, the top region also has the highest transvinylene measurement, but yields the lowest oxidation index.
As can be seen from the measurements above, there seems to be a slight trend in the data resulting in various peaks. The results show an increase in peak area and intensity around three specific wavelengths. It appears that as there is an increase in concentration of vitamin-E over the ten-year span, there is an increase in peak area around the Carbonyl section (around $1720 \text{ cm}^{-1}$). The corresponding Carbon-Hydrogen section (around $1370 \text{ cm}^{-1}$) also shows a steady increase in peak area. As the wavelength increases even further, it can also be observed that an increase in peak area in the trans vinylene also occurs around $965 \text{ cm}^{-1}$.

Now that the relationships between the three regions in each sample have been observed, now let’s look at the relationship and possible trend of all concentrations together.
The above graph shows the relationship of the concentration of vitamin-E and its corresponding Carbonyl levels. This plot focuses on comparing all controls and Nitrogen Gamma tested samples separately. It is shown that there is an initial decrease and final increase in the Carbonyl levels as the controls increase. However, there is a steady increase in the Carbonyl level between each of the Nitrogen Gamma tested samples. Now the relationship between each individual control and Nitrogen Gamma tested sample for each concentration of Vitamin-E will be observed in the figure below.
This figure shows the relationship of the concentrations of Vitamin-E and each of its controls and Nitrogen tested samples. As mentioned earlier, there is also a slight initial decrease in the Carbonyl group until the 1% Vitamin-E sample results. Beyond this point, there is a steady increase in the Carbonyl group resulting in the Nitrogen Gamma tested groups to have a higher level of Carbonyl.
The plot above shows the relationship of the concentration of Vitamin-E with the standard Carbon-Hydrogen Peak ($1370 \text{ cm}^{-1}$). This plot shows interesting results in the fact that the standard peak area for the control groups has a steady decrease from 0.5% Vitamin-E until 15% Vitamin-E is measured. The 15% Vitamin-E control and Nitrogen Gamma Irradiated group yielded the highest standard peak area amongst every other group. Likewise, the measurements will now be split into two groups (control and Nitrogen Gamma) and compared.
Figure 53: Comparisons for Vitamin-E Vs. Carbonyl Grouped by Vitamin-E Concentration

This plot shows the relationship of each individual sample. The results show an overall increase from 1% up to 15% Vitamin-E. There are a few deviations from 0% Vitamin-E to 0.5% Vitamin-E that needs further investigation.
This is a plot comparing all of the controls and Nitrogen Gamma tested samples separately. As can be seen, there is no obvious trend in the Trans Vinylene occurrence. Now, each sample will be compared separately in the figure below.

As a function of Vitamin-E, there is a slight trend in the amount of Trans vinylene present as the Vitamin-E Dosage increases when comparing all controls and Nitrogen Gamma tested samples separately. However, there is a slight irregularity with the 0.5% concentration, which shows no presence of Vitamin over the span of more than ten years. There also a slight increase of Trans Vinylene at 1% Nitrogen Gamma that appears to be more than the amount of Trans Vinylene at 10% Gamma Irradiated. Even though these cases occur, there is a clearer understanding when comparing each control to its corresponding Nitrogen Gamma tested sample as shown in the next figure.
This plot shows the relationship between the different concentrations of Vitamin-E and Trans Vinylene. The 0% Control has no Trans Vinylene present, which is to be expected since there is no vitamin-E Present in this sample. It would be best to also have the 0% Nitrogen Irradiated sample to be tested to see if there is any increase in Trans Vinylene, which in theory, should occur based off of the other samples that are tested, but because of the effects of Covid-19, this sample was unable to be tested. Despite the areas that have no Trans Vinylene at all, there is a steady increase in the occurrence of Trans Vinylene when comparing each control to its matching Nitrogen Irradiated sample as the Dosage of Vitamin-E increases as to be expected with the Vitamin-E molecules attaching to the double carbon bonds in the sample.
When comparing controls and Nitrogen Gamma samples separately, there seems to be no trend in the oxidation index. Every Vitamin-E Concentration fluctuates back and forth between samples. The 10% concentration tends to have the highest oxidation index in both groups, which should be studied further.
This plot yields interesting results. When comparing each concentration separately, the oxidation index decreases from 0% (assuming 0% Nitrogen Gamma would have a lower OI than the control) to 1% with a sudden increase in OI from 10% to 15%.

3.2: Experimental Results For UV/Vis Spectrophotometry:

In order to determine the molecular changes for each concentration of Vitamin-E, an average of the three samples for each concentration and variable (control and Nitrogen Gamma) were averaged out. First, the average peak and baseline for each sample were measured. For example, to find the average for 0.5% vitamin-E Control, the peaks and baselines for the three controls were measured. Next, the baseline is subtracted from the peak for each individual sample to get an average change in absorbance for each of the three control samples for 0.5% Vitamin-E. Once each sample has its individual change in absorbance, the three values are
averaged out to get one value for the average change in absorbance for 0.5% Vitamin-E Control. For example, let’s take this graph:

![Figure 58: Example UV-VIS Curve for Calculation](image)

This is an example plot of the 1% vitamin-E Nitrogen Gamma that was measured during this technique (results will be explained later in paper). The change in absorbance will be measured for sample 3 (green), since it’s the clearest curve. First, to find the change in absorbance, the peak and baseline will be found. Notice that the arrow at the top is not pointing at the true “peak” of the curve. This is because part of the curve that appears to be the “peak” may just be noise (these curves were smoothed). It is better to take an average peak, which is through the middle of the noise to get a better representation of the true peak. Here, the average peak is around 3. The same thing applies to the baseline. A line is drawn through the middle of the baseline to consider the noise and the average baseline is found to be around 1.24. Now, to get the change in absorbance, the average baseline is subtracted from the average peak. So, $3.0 - 1.24 = 1.76$. This leaves a change in absorbance with a value of 1.76. The same steps are applied to samples 1 and 2. The three changes in absorbance are then averaged to get one true change in absorbance for 1% Vitamin-E Nitrogen Gamma.
This is done for every Concentration of vitamin-E for both irradiated and non-irradiated samples to minimize the amount of error that could occur due to thickness inconsistency and to consider the crystallinity of the samples. The following graphs below show the spectrum of the three samples tested for each dosage of Vitamin-E for non-irradiated and Nitrogen Irradiated.

**0% Vitamin-E Control and Nitrogen Gamma**

![Wavelength vs. Absorbance](image1.png)  
**Figure 59: Comparisons for 0% Vitamin-E**  
![Wavelength vs. Absorbance](image2.png)  
**Figure 60: Comparisons for 0% 50 KGy**

On the 0% Vitamin-E Control plot, each sample had different baselines. Despite this being the case, samples 2 and 3 had roughly the same change in absorption due to the baseline to peak ratio. Sample 1 had the lowest change in absorption.

On the 0% Vitamin-E 50 KGy plot, sample 3 appeared to have the highest change in absorbance with sample 1 resulting in the lowest. Each sample also had different baselines in comparison to the control group.
Figure 61: Comparisons for 0% Vitamin-E 100 KGy

This plot of 0% Vitamin-E 100 KGy resulted in slightly similar peaks and baselines with a difference of change in absorption between each with a value of about 0.5.

0.5% - 15% Vitamin-E Control and Nitrogen Gamma

Figure 62: Comparisons for UV-VIS 0.5% Vitamin-E Control

Figure 63: Comparisons for UV-VIS 0.5% Vitamin-E Irradiated
The figures above show the plots for 0.5% Vitamin-E Control and Nitrogen Gamma Irradiated samples. The control samples 2 and 3 were quite similar than sample 1 as sample 1 had a much lower baseline, which yielded a much higher change in absorbance.

The 0.5% Vitamin Nitrogen Gamma deviated from sample to sample with ample 3 having the highest change in absorbance.

The 1% Vitamin-E Control had interesting results. Samples 2 and 3 had the same overall shape, yielding close to the same change in absorbance. Sample 1, however, did not get as high of a peak as samples 2 and 3, which resulted in a lower change in absorbance.

The 1% Vitamin-E Nitrogen Gamma plot yielded in an increase in the change in absorbance from sample to sample with sample 3 having the highest change in absorbance and sample 1 have the lowest change in absorbance.
The 10% Vitamin-E Control Plot shows that each sample has a common baseline with varying peaks. Sample 3 resulted in the highest change in absorbance. The 10% Vitamin-E Nitrogen Gamma sample has two very closely related absorption bands with sample 3 deviating from the other two. Samples 1 and 2 had the highest change in absorption.
The 15% Control plot shows similarities in the baselines of samples 2 and 3 with sample 1 being slightly lower. Sample 3 resulted in a higher change in absorbance with samples 1 and 2 having close to the same change in absorbance with a difference of .01.

Sample 3 in the 15% Nitrogen Gamma plot yielded the highest change in absorbance with sample 1 having the lowest change in absorbance differing from sample 2 by about 0.1.

![Figure 70: Comparisons for UV-VIS Vitamin-E Concentration Vs. Change in Absorbance](image)

The figure above shows the corresponding relationship of the concentration of Vitamin-E and the change in absorbance at each concentration of vitamin-E. Each measurement represents the average change in absorbance of three thinly cut samples from a bulk of Polyethylene containing the same concentration of vitamin-E. As can be seen, there is a steady increase in change in absorbance when comparing controls and Nitrogen Gamma irradiated samples.
separately with the 15% Vitamin-E Control and Nitrogen Gamma having the highest change in absorbance.

![Figure 71: Comparisons for UV-VIS Vitamin-E Concentration Vs. Change in Absorbance Grouped by Vitamin-E Concentration](image)

This is a plot that shows the average change in absorbance based off vitamin-E concentration. As seen in the previous figure, there is an increase in oxidation index between each individual control and Nitrogen irradiated sample for each vitamin-E Concentration.
DISCUSSION/CONCLUSION

Regarding the UV/Visible spectrophotometry, there was a continuous increase in absorbance as a function of vitamin-E. The change in absorbance for the UV/Visible Spectrophotometry had a consistent increase with varying dosages of vitamin-E among both the control and gamma-irradiated samples. The most significant observations of the study from the FTIR results were the oxidation (OI) measurements, which are indicative of oxidation which has occurred in the samples. There was a decreasing oxidation index in the UHMWPE samples; OI was greater in the non-Vitamin-E containing samples than in the samples containing 0.5% vitamin-E, for both non-irradiated and irradiated samples. This OI decrease is as expected, due to the antioxidant effect of vitamin-E. Unexpectedly, however, OI increased for the UHMWPE blend containing 10% Vitamin-E, up to 15% Vitamin-E. This apparent “pro-oxidant” observation will require further investigation. Studies have shown Vitamin-E (a-tocopherol) to have pro-oxidant effects in other materials (e.g., see Kontush et al., 1996); perhaps similar is occurring here for these UHMWPE samples. Still, stating such a conclusion is reversed until all other possible contributors can be thoroughly explored; Possibilities include the vitamin-E changing structure, or evaporating out of the UHMWPE, as these samples were aged for approximately 10 years, and little is known regarding the durations of storage. Although crosslinked medical grade UHMWPE containing Vitamin-E is a relatively “new” material, what happens to it over time is not well explored, especially for durations of 10 years or more; many future investigations are required to fully understand this material and what happens over time, a goal of which this paper contributes to.
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UV-Vis Absorption Spectroscopy - Theory,

[Link to teaching resource](https://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab1.htm#:~:text=Electronic transitions,the excitation of outer electrons.&text=Transitions involving p, s, and,Transitions involving charge-transfer electrons.

