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Effect of Antioxidants on Ultra High Molecular Weight Polyethylene (UHMWPE)

Clifford Schrader

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EFFECT OF ANTIOXIDANTS ON ULTRA HIGH MOLECULAR

WEIGHT POLYETHYLENE (UHMWPE)

(TITLE)

BY

Clifford Schrader

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YEAR

I HEREBY RECOMMEND THAT THIS THESIS BE ACCEPTED AS FULFILLING
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Abstract:

This thesis presents a study on the effects of antioxidants on the oxidative induction time (OIT), thermal behavior, and hardness property of ultra high molecular weight polyethylene (UHMWPE). The antioxidants were dissolved into methanol alcohol before the solution was mixed with UHMWPE powder. The mixture was degassed under vacuum, and then compression-molded into disks 1.25 in. in diameter.

Different antioxidants were evaluated at concentrations up to 0.6 percent. A 0.6 percent concentration was used to screen the effectiveness of various antioxidants. Effect of antioxidant concentration was investigated in the range between 0 and 0.6 percent. OIT was evaluated on UHMWPE with various antioxidants to understand the effects of antioxidants on oxidation resistance of the polymer. The experiments were performed using high pressure differential scanning calorimetry (HP DSC) with an isothermal temperature of 165 °C, and pure dry oxygen under a pressure of 500 psi. Regular differential scanning calorimetry (DSC) was used to evaluate the thermal behavior and changes in molecular structure of the polymer with antioxidants, in which a scanning rate of 10 °C/min. was utilized from room temperature to 200 °C. With the regular DSC, thermal stability of UHMWPE with various antioxidants was assessed from room temperature up to 300 °C. Durometer hardness (Type D) was tested on the polymer in order to understand changes in mechanical property and polymeric structure of UHMWPE due to antioxidants.

The OIT of UHMWPE was increased with the addition of antioxidants except β -carotene. Quercetin, at a concentration of 0.6 percent, was the most effective antioxidant, which increased the OIT 1133 percent. The effectiveness of antioxidant increased as

their concentrations increased in the tested range. The effectiveness can be arranged in descending order as: quercetin > BNX 1010 > GSPE > BHT > vitamin E > TBHQ > vitamin C > β -carotene. There was a weak synergy between BHT and vitamin E. A strong synergy was demonstrated between GSPE and quercetin.

Results indicated that the addition of antioxidants had very little or no effect on the thermal behavior of UHMWPE. This fact suggests antioxidants at the concentrations studied had little effect on the molecular structure of UHMWPE.

Thermal stability of UHMWPE was increased with the addition of antioxidants. The effectiveness of the antioxidants on thermal stability in descending order was: quercetin > BNX 1010 > vitamin E > GSPE > BHT > TBHQ > vitamin C.

Hardness test results determined that the addition of antioxidants did not significantly change or increase the hardness of UHMWPE, which indicates no significant cross-linking of the polymer.

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Table of Contents

	Page
1. INTRODUCTION	1
1.1 Statement of Research	3
1.2 Significance of Research	3
1.3 Definitions	4
1.4 Assumptions	5
1.5 Limitations	6
1.6 Delimitations	6
1.7 Hypothesis	7
 2. REVIEW OF LITERATURE	 8
2.1 Significance of Joint Replacement	8
2.2 Problems Associated with Joint Replacement	8
2.3 Vitamin E and UHMWPE	10
2.4 Natural and Synthetic Antioxidants	10
2.5 Thermal Analysis	14
2.6 Method of Evaluation for Oxidation Resistance	15
2.7 Method of Hardness Evaluation	16
 3. METHODOLOGY OF THE RESEARCH	 18
3.1 Materials	18
3.2 Procedure	19

3.3 Thermal Behavior Evaluation Using Differential Scanning	
Calorimetry (DSC)	21
3.4 Thermal Stability Evaluation Using Differential Scanning	
Calorimetry (DSC)	22
3.5 Oxidative Induction Time (OIT) Evaluation	22
3.6 Durometer Hardness Evaluation	23
4. PRESENTATION AND INTERPRETATION OF DATA	25
4.1 Effects of Various Antioxidants on Ultra High Molecular Weight	
Polyethylene (UHMWPE)	25
4.2 Effects of Various Antioxidants on Durometer Hardness of	
UHMWPE	28
4.3 Effects of Various Antioxidants on the Thermal Behavior of	
UHMWPE	30
4.4 Effect of Antioxidant Concentration on OIT of UHMWPE	34
4.5 Effects of Antioxidant Concentration on Hardness of UHMWPE	38
4.6 Effects of Antioxidant Concentrations on the Thermal Behavior	
of UHMWPE	39
4.7 Testing for Synergy Between Antioxidants	41
4.8 Effects of Antioxidant Combinations on Hardness	43
4.9 Effects of Antioxidant Combinations on the Thermal Behavior	
of UHMWPE	44

5.	CONCLUSION	46
	RECOMMENDATION FOR FURTHER RESEARCH	47
	REFERENCES	48

List of Tables

Table	Page
1 Physical Properties of Antioxidant	19
2 Oxidative Induction Time (OIT) of Ultra High Molecular Weight Polyethylene (UHMWPE) with 0.6 Percent Antioxidant	28
3 Average Durometer Hardness at 1 Second	29
4 Differential Scanning Calorimeter (DSC) Results of UHMWPE with 0.6 Percent Antioxidant	32
5 Oxidation Temperatures of UHMWPE with 0.6 Percent Antioxidant	34
6 OIT of UHMWPE with 0.1, 0.2, 0.4, and 0.6 Percent Antioxidants (OIT [min]/Net Percent)	35
7 Average Durometer Hardness at 1 Second as a Function of Antioxidant Concentrations	38
8 Differential Scanning Calorimeter (DSC) Results	40
9 OIT of UHMWPE with Combinations and Individual Antioxidants at 0.2 Percent	42
10 Average Durometer Hardness at 1 Second of Samples with Antioxidant Combinations	44
11 Differential Scanning Calorimeter (DSC) Results of UHMWPE with Combinations of Antioxidants	45

List of Figures

Figure		Page
1	Processing parameters for compression molding	21
2	Oxidative Induction Time (OIT) thermal curve of ultra high molecular weight polyethylene with 0.6 percent GSPE	26
3	Regular Differential Scanning Calorimeter (DSC) graph showing both endothermal and exothermal curves	31
4	Oxidative induction time response to antioxidant concentrations	37

Chapter I

Introduction

The aging of America's population and advances in orthopedic surgery have made joint replacement surgery an effective orthopedic procedure. It is estimated that, in the United States alone, 400,000 knee joint replacements are performed annually (McCullen, Geoffrey, & Miller, 1998). This procedure allows people to remain productive and self-sufficient instead of needing costly long-term care.

One of the major problems with joint replacement is that the polymer commonly used in this application, ultra high molecular weight polyethylene (UHMWPE), is susceptible to wear. Heavier and more active patients are generally at the highest risk of premature joint failure. Due to design, loading, and arc of travel, knee joints followed by the hip are the most susceptible to complications related to wear particulates (Young, Cheng, Lee, Chen & Huang, 1998). On the articulating surfaces of replacement joints millions of submicron plastic particles are generated. Nolan and Phillips (1996) have reported that tiny and, previously unidentifiable, products of movement are generated, not only within the articulation but also through much smaller degrees of movement at modular interfaces, and at prosthesis-cement, cement-bone, or prosthesis-bone interfaces.

The degree of adverse reaction to polyethylene debris is directly related to the size, shape, and volume of particles. Wear particles have also been found in the lymphatic tissues which, indicates that they can translocate throughout the body causing effects not fully understood or researched at this time (Nolan & Phillips, 1996).

After artificial joints are manufactured, they are routinely sterilized. Gamma radiation is the most effective way to sterilize artificial joints. However, it has recently

been ascertained that the premature *in vivo* wear of UHMWPE can be attributed to the sterilization process by gamma radiation. Long-term performance of an artificial joint is compromised by post irradiation oxidative degradation of UHMWPE.

Free radicals are produced in a polymer when highly charged subatomic particles, from a radiation source, break polymer chains. Gamma irradiation of UHMWPE leads to the formation of long-lived free radicals, which react with oxygen. As Premnath, Harris, Jasty, and Merrill (1996) reported, diffusion of oxygen, occurring over months or years, controlled by the permeability characteristics of the polymer, resulted in progressive oxidation, breaking of polymer chains, alteration of the crystalline structure, and deterioration of mechanical properties of the polymer.

One possible method of decreasing the effect of gamma radiation and its associated oxidization on UHMWPE is to add stabilizing substances to the polymer. One major challenge of this approach is to find additives that are both effective and acceptable to the biomedical community. One group of substances that may be suitable to this application are antioxidants. Antioxidants are compounds that can be either synthetically manufactured or extracted from fruits, vegetables, grains, and other plants. Some antioxidants are commonly used as food preservatives or in cosmetics. Others are used in more industrial applications like paint additives, electrical wire insulation, plastic pipe, and rubber products.

Research has been conducted on the effects of antioxidants on stabilizing and increasing the useful life of various vegetable oils and animal fats. Dougherty of Eastman Chemical Company (1993) has demonstrated that as little as 0.002 percent of tertiary butylhydroquinone (TBHQ) added to lard increased the time of oxidation by a

factor of 12. Dougherty's research has also demonstrated that a synergy existed between TBHQ and ascorbic acid (vitamin C) in lard and between TBHQ and tocopherols (vitamin E) in menhaden oil.

Tomita, Kitakura, Onmori, Ikada, and Aoyama (1999) demonstrated that the addition of vitamin E to gamma-sterilized UHMWPE significantly reduced crack formation and particle generation due to wear. They stated that the reason vitamin E reduced crack formation was not positively determined. Effects such as enhanced cross-linking or reduced micro pore might occur by adding vitamin E. A small amount of vitamin E was effective because it was compounded in UHMWPE powder and may be distributed at the grain boundaries. The most effective level of vitamin E used in this research was 0.3 percent. There has been no research found to indicate that antioxidants have been evaluated as a means of stabilizing UHMWPE.

1.1 Statement of Research

The purpose of this research is to determine if incorporating antioxidants into UHMWPE would increase the polymer's resistance to oxidization and thereby contribute to prolonging the life of the polymer part of artificial joints.

1.2 Significance of Research

This research facilitates an understanding of effects of chosen antioxidants on oxidation resistance of UHMWPE. The results from this research will benefit orthopedic prosthesis manufacturers, orthopedic surgeons, and patients who require joint

replacement. This research will also be of interest to engineers, scientists, and technologists who work in the areas of materials science and applications.

1.3 Definitions

For better understanding of this research the following terms require clarification:

Antioxidant:	A substance that inhibits reactions with oxygen or peroxides.
Articulating:	The movement at a joint or junction between bones or cartilages in the skeleton of a vertebrate.
BHT:	Butylated hydroxytoluene, a low molecular weight food grade synthetic antioxidant.
Free Radical:	A molecule that contains an unpaired electron and is unstable (Strong, 1996).
GSPE:	Grape seed proanthocyanidin extract, a polyphenolic bioflavonoid antioxidant extracted from grape seeds.
Inflammation:	A local response to cellular injury that results in redness, heat, and pain.
Oxidation:	The process of reaction with oxygen (Strong, 1996).
OIT:	Oxidative Induction Time, an index determining the resistance to oxidation of hydrocarbon materials.
Plastic:	A polymeric material either thermoplastic or thermoset.
Polymer:	A chemical compound formed by polymerization and consisting of repeating units (monomers).

Irradiation:	The act of subjecting an object to radiant energy in the form of waves or particles.
Quercetin:	A natural flavonoid antioxidant that has been isolated from many plants.
Sterilization:	The process of making an object free from living microorganisms.
TBHQ:	Tertiary butylhydroquinone, a synthetic phenolic antioxidant.
Vitamin E:	Tocopherol, fat-soluble phenolic compound with varying degrees of antioxidant vitamin E activity obtained from germ oils or by synthesis.
UHMWPE:	Ultra high molecular weight polyethylene, a polyethylene that has extremely long polymer chains (Strong, 1996).

1.4 Assumptions

In this research the following assumptions were made:

1. Antioxidants used in this research are close to their original condition and in compliance with industry standards.
2. Montell 1900 UHMWPE is of similar type and performance to the polymers normally used in replacement joints.
3. Oxidative induction time (OIT) test is an accurate predictor of the antioxidants' effects on stabilizing UHMWPE.
4. Antioxidants were evenly distributed throughout the polymer matrix.
5. Antioxidants were not degraded significantly during processing.

1.5 Limitations

The findings of this research were limited by the following parameters:

1. The quality of UHMWPE and antioxidants is controlled by suppliers.
2. Human error and accuracy of the testing equipment may affect test results.
3. Characteristics of UHMWPE and antioxidant combinations may be affected by the compression molding process.
4. Changes in ambient temperature and the associated rate of cooling of the compression molded specimens may affect research results.

1.6 Delimitations

The research was delimited to the following parameters:

1. The type of UHMWPE used in this research was Montell 1900, which was supplied by Biomet Inc. of Warsaw, Indiana.
2. The antioxidants used in this research included the following:
 β - carotene, BHT (butylated hydroxytoluene), GSPE (grape seed proanthocyanidin extract), quercetin, TBHQ (tertiary butylhydroquinone), vitamin C (ascorbic acid), vitamin E (α -tocopherol), and BNX 1010 (tetrakis [Methylene-3(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate] methane).
3. Individual and combinations of antioxidants did not exceed 0.6 percent by weight.
4. Oxidative induction time (OIT) test was selected for evaluating oxidation resistance of UHMWPE.

5. Oxidative induction time (OIT) evaluations were performed using a high pressure differential scanning calorimeter (DSC) (TA Instruments, DSC 2910).

6. Regular differential scanning calorimeter (DSC) evaluation was used to determine thermal behavior and thermal stability.

7. Hardness testing was performed with a Shore Model 80 durometer utilizing a type 412D indenter.

1.7 Hypothesis

Incorporating a variety of antioxidants individually, at various concentrations, and in combination into compression molded UHMWPE specimens will affect oxidative induction times, thermal stability, polymeric structure, and hardness.

Chapter II

Review of Literature

The review of literature focuses primarily on the research associated with:

1. Joint replacement
2. Sterilization and oxidation of UHMWPE
3. Effect of vitamin E on polyethylene joint components
4. Potential effectiveness of various other antioxidants
5. Methods of evaluation

2.1 Significance of Joint Replacement

Approximately 400,000 knee replacement surgeries are performed annually in the United States (McCullen, Geoffrey, & Miller, 1998). This number is expected to increase in the future due to the aging of population in America and many other parts of the world. Although the operation is expensive (approximately \$25,000), it allows people to resume working or taking care of themselves rather than depending upon long-term care.

2.2 Problems Associated with Joint Replacement

Goldman, Lee, Gronskey, and Pruitt (1996) stated that UHMWPE has been used as a replacement for damaged cartilage for over 30 years. Suitability of the polymer to this application is due to its exceptional engineering performance, including superior wear resistance and low friction. Unfortunately, *in vivo* performance has been disappointing due to pitting, delamination and wear.

Nolan and Phillips (1996) indicated that particulate debris from replacement joint wear was a very serious problem. The wear resulted in loosening of articulating parts, and the debris cause complications. Inflammation of the joint is a direct result of the presence of debris. This inflammation causes damage and loosening of the bone – prostheses interface, which leads to failure of the implant. Wear debris have also been found in the lymph nodes, which indicates they can translocate throughout the body.

Costa et al. (1997) studied the relationship between UHMWPE oxidation and sterilization methods using gamma radiation and ethylene oxide. They concluded that the energy level of gamma-radiation is five orders higher than that of carbon bonds in polymer molecules. The breaking of polymer molecular chains results in generation of free radicals, which leads to oxidation and accelerated wear. The ethylene oxide method of sterilization did not demonstrate this kind of problem. Unfortunately, ethylene oxide is a highly toxic material that can leave a residue on the implant.

Radiation has been identified as a major contributing factor to the mechanical breakdown of the polymer (Goldman et al. 1996). Premnath, Harris, Jasty, and Merrill (1995) studied the oxidation problem associated with gamma sterilized UHMWPE. Their results suggested that the oxidation rate of UHMWPE was directly related to the exposure time and oxygen content of the environment. This finding indicates that it is very important to store gamma-radiated polymers in a vacuum or an inert environment and that orthopedic prosthesis may have a limited shelf life.

Young et al. (1998) investigated the failure of UHMWPE knee inserts of clinically retrieved components. Their results indicated that the thermal effect of friction heat on UHMWPE accelerated the oxidation process resulting in material damage.

Therefore, it was concluded that research related to improving the performance of artificial joint prostheses should attempt to minimize the thermal effects and oxidation upon articular components.

2.3 Vitamin E and UHMWPE

Vitamin E or α -tocopherol is considered to be an effective antioxidant for neutralizing free radicals generated in the human body (Papadimitrakou, 1999). Data by Dougherty (1993) indicated that tocopherols were very stable at high temperatures. This was ascertained using the Schaal Oven Stability test on fried potato chips. Tocopherol was also proven to exhibit the greatest heat stability when compared with BHA, BHT, and TBHQ. This was determined by exposing the antioxidants to increasingly higher temperatures and measuring the resultant vapor pressure. Research by Tomita et al. (1999) indicated that the addition of vitamin E to gamma irradiated UHMWPE halted the development of surface cracking and particulate debris generation in *in vitro* testing. It was determined that gamma irradiation exposure resulted in hardening of the grain boundary of UHMWPE. This hardening resulted in cracking and wear debris generation when subjected to a sliding fatigue test. It is believed that the addition of vitamin E to UHMWPE prevents crack propagation due to reduced hardness of grain boundaries making this antioxidant a promising additive to UHMWPE.

2.4 Natural and Synthetic Antioxidants

Cadenas and Packer (1996) stated in their "Handbook of Antioxidants" that β -carotene may be a very effective antioxidant or protective compound for human

photosensitivity disorders. Papas, in his book "Antioxidant Status, Diet, Nutrition, and Health," stated that β -carotene was one of the most potent quenchers of singlet oxygen and was an effective antioxidant. However, Henry, Catignani, and Schwartz (1998) concluded that β -carotene had no antioxidant effect on the stability of safflower seed oil during heat-catalyzed oxidation in a comparison test with α -tocopherol (vitamin E) and butylated hydroxytoluene (BHT). They also determined that there was no cooperative interaction between α -tocopherol and β -carotene in delaying the onset of oxidation.

Butylated hydroxytoluene (BHT) was demonstrated to be effective in the suppression of oxidation in safflower oil during heat-catalyzed oxidation by Henry et al. (1998). This study compared BHT with β -carotene, and concluded that β -carotene had no significant effect on prolonging the onset of oxidation, while BHT was very effective. *In vitro* testing by Jiyun, Tai, and Hopkins (1997) also demonstrated that BHT has antioxidant activity in the cardiovascular system. Dougherty (1993) reported the effect of antioxidants on stabilizing castor oil using the Active Oxygen Method (AOM) at a test temperature of 97.8°C. It was shown that the antioxidant strength of BHT is equal or superior to tocopherols in lard and castor oil. Caution, however, must be exercised when using the compound as an antioxidant in food products because it has demonstrated potentially toxic effects at very high levels (Papas, 1999).

Bagchi, Garg, Krohn, and Bagchi (1997) studied the oxygen free radical scavenging abilities of Grape Seed Proanthocyanidin Extract (GSPE), vitamin C, and vitamin E succinate (VES). This research was done *in vitro* using superoxide anion and xanthine oxidase, as catalyst, to initiate the production of hydroxyl radicals. The oxygen free radical scavenging abilities were determined by chemiluminescence and cytochrome

c reduction. Results indicated GSPE was superior to both vitamin C and E for scavenging oxygen free radicals. It was concluded that GSPE exhibited 78-81% inhibition of superoxide anion and hydroxyl radical. Whereas, vitamin C inhibited these two oxygen free radicals by approximately 12-19%, and VES inhibited the two radicals by 36-44%. Ray, Kumar, and Bagchi (1999) studied the damage to internal organs that result from oxidative and stress related illnesses. This was done by injecting mice with acetaminophen, a substance known to cause oxidative liver damage. Some mice were preexposed to GSPE seven days before being injected with the acetaminophen. The mouse livers were evaluated by Western blot analysis. Results indicated that 7-day GSPE preexposure induced dramatic protection and markedly decreased liver injury. Mice not preexposed to GSPE suffered a mortality rate of 28-44 percent while all those exposed to GSPE lived.

Hall and Cuppet (1993) compared the effectiveness of Tertiary Butylhydroquinone (TBHQ) and rosemary oleoresin (RO) on stabilizing soybean oil against light-induced oxidation. Oxidation levels were determined by using the modified spectrophotometric method of the Association of Official Analytical Chemists. Results of this study indicated that TBHQ treatment had significantly greater antioxidant activity than RO. Dougherty of the Eastman Chemical Company (1993) has also published research on the effectiveness of TBHQ in stabilizing both animal and vegetable oils. Active Oxygen Method (AOM) was used to measure the relative effect of antioxidants in fats and oils that were liquid at the test temperature of 97.8°C. In comparison with other synthetic and natural antioxidants, TBHQ demonstrated superior heat stability and antioxidant

effectiveness in lard, soybean oil, and menhaden oil. It was also determined that a synergy existed between TBHQ and tocopherols for stabilizing lard.

Reports regarding the use of vitamin C (ascorbic acid), as an individual antioxidant, are not very encouraging. Research on peroxynitrite scavenging by Balavoine & Geletii (1999) indicated that vitamin C may be an effective antioxidant due to its ability to generate antioxidants rather than trap radicals directly. Ascorbic acid (vitamin C) has been found to have a synergy with vitamin E (Papad, 1999). Research by Han, Yi, and Shin (1991) using vitamins C and E to stabilize fish oil has demonstrated that there is a strong synergy between these two compounds in retarding oxidation. However, in certain circumstances at low concentrations vitamin C can also act as a prooxidant (Cadenas, 1996).

Quercetin is a natural phenolic antioxidant. According to research by Chen and Ahn (1998), it has demonstrated superior antioxidant effectiveness in comparison to other natural phenolic antioxidants in flax oil exposed to ultraviolet radiation. The evaluation method involved preparing an oil emulsion using flax oil and acid-reactive substances. This research determined that the antioxidant activities of the six phenolics against UV-induced lipid oxidation were as follows: quercetin > rutin = caffeic acid = ferulic acid = sesamol > catechin. Quercetin was also the most effective antioxidant in a study by Balavoine & Geletii (1999) comparing different polyphenols effectiveness for scavenging oxygen free radicals. This research used peroxynitrite as a source of radicals with pyrogallol red (dye) as a detecting molecule. The tests were conducted by mixing the peroxynitrite, pyrogallol red dye and antioxidants with water. The strength of dye was measured with an UV-Vis spectrometer. Effectiveness of the antioxidant was determined

by the presence of the dye. Research by Jiyun et al. (1997) examined the antioxidant effectiveness of quercetin, rutin, and BHT on tissue samples. Effectiveness of the antioxidants was measured using the xanthine-xanthine oxidase luminol and the alkaline sodium dithionate chemiluminescence systems. Their studies showed that *in vitro* all compounds had some degree of anti-free radical activity, but quercetin was the most potent.

BNX 1010 (tetrakis [Methylene-3(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate] methane), is an antioxidant used primarily for industrial polymers. It is a high molecular weight hindered phenolic antioxidant that exhibits excellent heat stability and good compatibility with most polymers (Mayzo, Inc., 1994). No research has been found to indicate that the above antioxidants have been used to improve oxidation resistance of UHMWPE.

2.5 Thermal Analysis

Thermal analysis is the generic term used for measurement techniques traditionally used to determine changes in material properties with temperature. Differential scanning calorimetry (DSC) is the most widely used thermal analysis technique. It is a technique which measures heat flow into or out of a material as a function of time or temperature (Foreman, Lundgren, & Hill, n. d.). The results of DSC analysis provide information about phase changes (amorphous and crystalline transitions) as well as chemical changes (degradation and reactions).

DSC analysis of polymers provides empirical data useful to determine changes in molecular weight, molecular weight distribution, and crystallinity. Melt temperatures in

general increase as molecular weight increases. Melt on-set temperatures increase or decrease in relation to changes in molecular weight distribution. Polymer crystallinity is related to the amount of heat needed (heat of fusion or enthalpy) to melt a polymer. The crystallinity of a polymer is equal to its heat of fusion divided by the heat required to melt a 100 percent crystalline sample. For UHMWPE, the heat required to melt a 100 percent crystalline specimen is 290 J/g.

Both the average molecular weight and molecular weight distribution can significantly affect some key physical and mechanical properties of a polymer such as tensile strength, impact toughness, creep resistance, and melting temperature. A higher molecular weight increases all of these mechanical properties, due to increased entanglement or wrapping of polymer chains around each other. Crystallinity can affect many physical properties with the most important being tensile strength. The degree of crystallinity is influenced by the manner in which a polymer is cooled from the melt. Slow cooling allows the crystalline regions to organize while there is still movement amount the chains and, therefore, favors the formation of crystallinity (Strong, 1996).

2.6 Method of Evaluation for Oxidation Resistance

Oxidative induction time (OIT) measurement is an accelerated thermal-aging test, which provides a quantitative assessment of the material tested. It is determined by the thermo-analytical measurement of the time interval to the onset of exothermic oxidation of a material at a specified temperature in an aerobic or pressure oxygen atmosphere. The onset of oxidation is signaled by an abrupt increase in the sample's evolved heat or

temperature, which is taken as the endpoint for the OIT measurement (Blaine, Lundgren, & Harris, 1997).

The American Society for Testing and Materials (ASTM) has approved the OIT test as a method of simulating accelerated aging. It provides a means by which the resistance to oxidation of a variety of hydrocarbon materials can be compared. Applicable materials would include: polymers used for pipe or wire insulation, oils and greases used for lubricants or fuel, and various edible vegetable and animal oils and fats. This test consists of heating the specimen to an elevated temperature in the presence of oxygen in a differential scanning calorimeter (DSC) until the polymer specimen has exceeded its differential temperature peak.

It has long been known that the effectiveness of antioxidants, as measured by the OIT at high temperatures, may differ as a function of temperature. This may be due to a loss of antioxidant as a result of volatilization at high temperatures. It is therefore considered advantageous to move the OIT test temperature closer to the actual use temperature to avoid some of these difficulties. Further, as additive packages have improved, OIT values have become progressively longer. In order to shorten the analysis time and to reduce test temperatures, increasing use is being made of pressure DSC to accelerate the measurement at lower temperatures.

2.7 Method of Hardness Evaluation

The American Society for Testing and Materials (ASTM) has approved the Durometer Hardness test as a method of determining hardness based on either initial indentation or indentation after a specific period of time, or both. This test is based on

the penetration of a specific type of indenter when forced into the material under specified conditions. The indentation hardness is inversely related to the penetration and is dependent upon the elastic modulus and viscoelastic behavior of the material. This test method is an empirical test intended primarily for control or comparison purposes (American Society for Testing and Materials [ASTM], 1994).

Chapter III

Methodology of the Research

3.1 Materials

For this research, ultra high molecular weight polyethylene (UHMWPE) Montell 1900 was provided by Biomet Inc. (Warsaw, IN) in fine granular form. Antioxidants butylated hydroxytoluene (BHT) and tetrakis [Methylene-3(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate] methane (BNX 1010) were donated by Marzo Inc. (Norcross, GA). Ascorbic acid (vitamin C), β -carotene, quercetin and α -tocopherol (vitamin E) were purchased from Sigma Chemical Co. (St. Louis, MO). Grape seed proanthocyanidin extract (GSPE) was provided by InterHealth Nutraceuticals (Concord, CA). Tertiary butylhydroquinone (TBHQ) was donated by Eastman Chemical Products (Kingsport, TN).

Physical properties of the antioxidants are listed in Table 1.

Table 1

Physical Properties of Antioxidants

Antioxidant	Molecular Weight	Melting Point (°C)	Material Characteristics
β -carotene	536.85	NA	Dark Red Powder
BHT (butylated hydroxytoluene)	220.34	70°C	White Crystals
BNX 1010 (tetrakis [Methylene-3(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate]methane)	1177.7	110-125°C	White Powder
GSPE (grape seed proanthocyanidin extract)	NA	NA	Brown Powder
Quercetin	338.3	NA	Yellow Powder
TBHQ (tertiary butylhydroquinone)	166.2	128°C	White Powder
Vitamin C (ascorbic acid)	176.12	190-192°C	White Crystal Powder
Vitamin E (α -tocopherol)	530.76	76-77°C	High Viscosity Brown Oil

3.2 Procedure

Test specimens were produced by compression molding a mixture of UHMWPE with various antioxidants. The first step was to weigh the UHMWPE and antioxidant using a Denver Instrument M-220D electronic balance. The antioxidant was placed into a 2-cup container with 20 mL of methyl alcohol and agitated until totally dissolved. Methyl alcohol was used as a solvent to facilitate the incorporation of antioxidants into UHMWPE. UHMWPE was added to this solution and mixed using a kitchen mixer for 7 to 10 minutes with the sides of the container scraped down to ensure a homogenous mixing. After blending, the mixture was placed into a desiccator and a vacuum was

pulled to remove all solvent and moisture. The mixture was then sealed in a polyethylene bag with a KF-200H impulse sealer and stored at -10°C .

Batch size was twenty grams, with an initial antioxidant concentration of 0.6 percent. Based upon previous research, this concentration was considered the maximum antioxidant level for this application. Thus, 0.6 percent was used initially to screen the effectiveness of antioxidants. Antioxidants that demonstrated some effectiveness in prolonging the onset of oxidation were tested at lower concentrations of 0.1, 0.2, and 0.4 percent to fully evaluate their performance as a function of concentrations. Antioxidants were also tested in combination to determine if there was any synergy in their performance. Combinations were tested at individual levels of 0.2 percent.

To begin compression molding, a bag of UHMWPE/antioxidant mixture was removed from the freezer and allowed to reach ambient temperature. The bag was then opened and 1.5 grams of material was weighed on the electronic balance. This material was then transferred into a mold and compression molded.

Figure 1 illustrates the temperature and pressure profiles for the compression molding. The mold was first heated to 120°C with zero pressure. Upon reaching 120°C , the pressure was increased and kept at 750 psi for 2 minutes. After the 2 minutes the pressure was decreased to 0 and then increased to 1000 psi for 1 minute. The mold temperature was then increased to 220°C and the pressure was decreased to 500 psi for 1 minute. Next, the power to the mold heater was terminated and the mold allowed to cool. When the mold temperature had cooled to 150°C , the pressure was increased to 1000 psi. This pressure was maintained until the mold cooled to near ambient temperature and the specimen removed from the mold. This process produced a specimen that was 1.25

inches in diameter by approximately 0.1 inches thick with a weight of 1.5 grams. These polymer discs were placed in labeled envelopes and stored in a desiccator in a nitrogen atmosphere until testing.

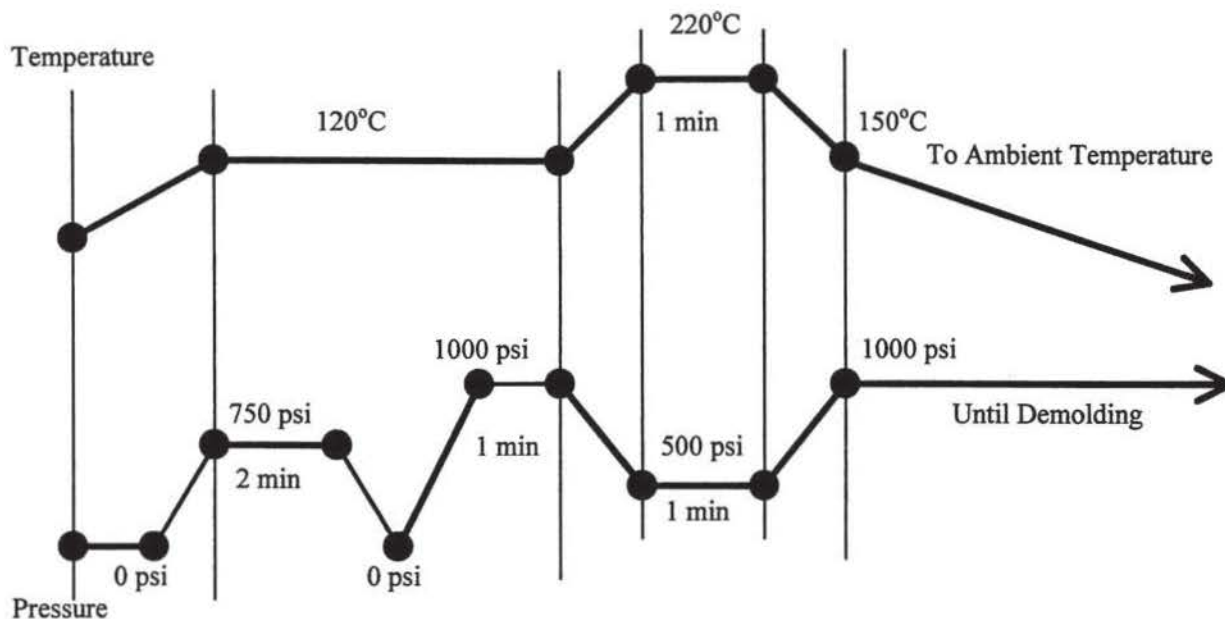


Figure 1 Processing parameters for compression molding

3.3 Thermal Behavior Evaluation Using Differential Scanning Calorimetry (DSC)

In order to determine if the addition of antioxidants had any effect on the molecular structure of UHMWPE, regular differential scanning calorimetry analysis was used. This evaluation was performed with a TA Instruments DSC 2910 differential scanning calorimeter (DSC) with a standard test cell. A scanning rate of 10°C/min. from room temperature to 200°C, with a nitrogen flow of 50mL/min. was used.

To perform the test, a polymer sample of 3mg \pm 0.2mg was cut from a compression molded specimen. This sample was placed in an aluminum pan, covered with a lid, and the lid crimped into place. The sample pan was placed on the front platform of the test cell with an empty pan placed on the rear platform as a reference.

Upon completion of the test, the nitrogen gas was then turned off, the sample pan removed from the DSC cell, and the data analyzed.

3.4 Thermal Stability Evaluation Using Differential Scanning Calorimetry (DSC)

DSC testing was performed to determine the effect of antioxidants upon the oxidization temperature of UHMWPE. This evaluation was also performed with a TA Instruments DSC 2910 differential scanning calorimeter (DSC).

These tests were performed using a standard DSC test cell, with a scanning rate of 10°C/min. from room temperature to 300°C, with no shielding gas. It was discovered that test specimens would not oxidize, if enclosed in a covered pan in a nitrogen environment under the maximum test temperature of 300°C.

To begin the thermal stability test, a polymer sample of 3mg \pm 0.2mg was cut from a compression molded specimen. The sample was placed in an uncovered aluminum pan and placed on the front platform of the test cell with an empty pan placed on the back platform as a reference. The test cell was then closed and the test executed in regular DSC mode with a scanning rate of 10°C/min. up to 300°C when the test was terminated. The sample pan was then removed from the test cell and the data analyzed.

3.5 Oxidative Induction Time (OIT) Evaluation

In order to simulate accelerated aging of the polymer/antioxidant specimens, oxidative induction time (OIT) test was conducted. OIT is a very useful way of comparing the relative resistance to oxidation for a variety of hydrocarbon materials.

This test was performed with a TA Instruments DSC 2910 scanning differential calorimeter (DSC).

In order to keep test times from being excessively long, an oxygen charged pressure cell was utilized. For this research, the OIT test was performed with the following test parameters: isothermal temperature of 165° C, pressure DSC cell with pure dry oxygen at a pressure of 500 psi, and sample size of 3mg \pm 0.2 mg. These three factors are very critical to the test accuracy and must be accurately maintained.

To perform the test, a polymer sample of 3mg \pm 0.2mg was cut from a compression molded specimen and placed into an aluminum pan. The sample pan was then placed on the front platform in the test cell. An empty pan was placed as a reference on the rear platform. The cell was then pressurized to 500psi with pure dry oxygen. The test was conducted by equilibrating to an isothermal temperature of 165°C and continued until an oxidation exotherm was observed on the thermal analyzer. After the test was completed, the pressure was slowly released by opening the pressure release valve on the pressure cell. The induction time was determined from the “extrapolated onset” in which tangents were drawn at the point of maximum rate of oxidation and the baseline prior to the oxidation. Their intersection was taken as the endpoint for the OIT measurement (Blaine, Lundgren, & Harris, 1997).

3.6 Durometer Hardness Evaluation

To determine if the addition of antioxidants has any effect on the mechanical properties of UHMWPE, Durometer Hardness was tested. Comparative hardness testing

is a method useful to determine if a polymer has undergone a change in its molecular structure resulting in differing levels of cross-linking.

For this research, hardness testing was performed with a Shore Model 80 Durometer with a type 412D indenter. The specimens tested were compression molded disks of 1.25 inches in diameter by 0.2 inches in thickness. All hardness measurements were taken after one second of compression by the indenter.

CHAPTER IV

Presentation and Interpretation of Data

This chapter presents the effects of antioxidants on the oxidative induction time (OIT), Durometer hardness, thermal behavior, and thermal stability of ultra high molecular weight polyethylene (UHMWPE).

4.1 Effects of Various Antioxidants on Ultra High Molecular Weight Polyethylene (UHMWPE)

Researchers have demonstrated that the selected antioxidants had certain effectiveness on various animal, vegetable, or petroleum oils at varying concentrations using different methods of evaluation. This makes it difficult to predict the effectiveness of antioxidants on ultra high molecular weight polyethylene (UHMWPE). As a first step of this study, antioxidants were screened at a concentration of 0.6 percent to identify their preliminary effectiveness on oxidative induction time (OIT) of UHMWPE. The OIT test was performed at an isothermal temperature of 165°C, with pure dry oxygen under a pressure of 500 psi.

Figure 2 illustrates a typical OIT thermal curve of UHMWPE with 0.6 percent GSPE. Heat flow (ΔH) is shown on the vertical axis and the time (Δt) on the horizontal axis.

The measurement is made by determining the time interval to the onset of exothermic oxidation. The onset of oxidation is signaled by an abrupt increase in the sample's temperature. It is noted that the OIT was approximately 88.5 minutes for UHMWPE with 0.6 percent GSPE.

Sample: UHMWPEGSP0.006
Size: 3.2000 mg
Method: OIT FOR UHMWPE
Comment: UHMWPE 0.006 GSPE

DSC

File: CS-PE6SPE0.006
Operator: CLIFF
Run Date: 5-Feb-00 14:03

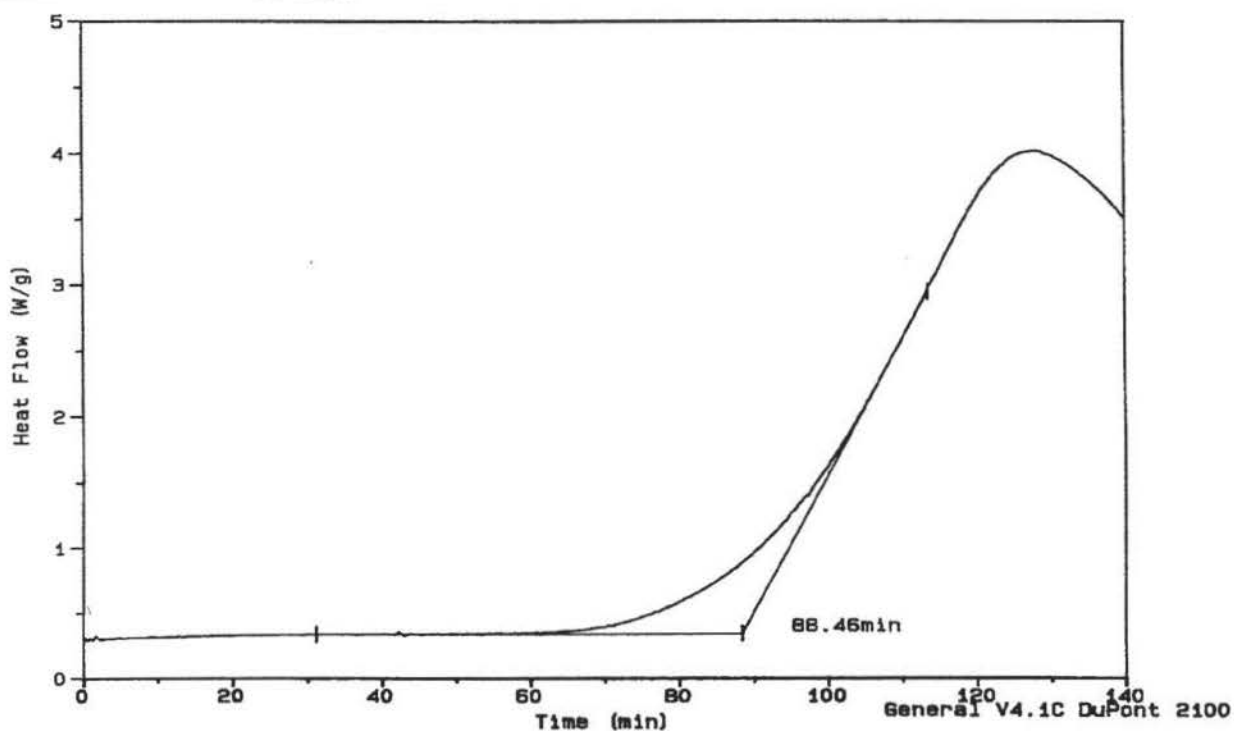


Figure 2 Oxidative Induction Time (OIT) thermal curve of ultra high molecular weight polyethylene with 0.6 percent GSPE

Table 2 displays the OIT results of UHMWPE mixed with 0.6 percent of various antioxidants. The OIT of pure UHMWPE was 24 min, which served as a baseline for the comparative study. It was noted that the OIT of polymer mixed with β -carotene was 18.5 minutes, or 5.5 minutes shorter than the pure UHMWPE. This fact suggests that β -carotene is not an antioxidant, but a pro-oxidant for UHMWPE.

According to Table 2, quercetin was the most effective antioxidant with an OIT of 296 minutes, or 272 minutes longer than pure UHMWPE. This represents an increase of 1133 percent in OIT from UHMWPE without any antioxidants. The effectiveness of the studied antioxidants at a concentration of 0.6 percent could be arranged in descending order as follows: quercetin > BNX 1010 > GSPE > BHT > vitamin E > TBHQ > vitamin C > β -carotene.

Based upon the OIT results, β -carotene was deemed ineffective for oxidation resistance improvement of UHMWPE and therefore received no further study. BNX 1010 is an industrial antioxidant currently used in many polymers. It was used as a control base only and did not receive any additional study at lower concentrations. Further study was performed on the other antioxidants to understand their effectiveness as a function of their respective concentrations.

Table 2

Oxidative Induction Time (OIT) of Ultra High Molecular Weight Polyethylene (UHMWPE) with 0.6 Percent Antioxidant

Antioxidant	OIT (min)	Net Effect of Antioxidant on OIT (min)/%	Ranking
Pure UHMWPE	24	None	
β -carotene	18.5	-5.5/-23	8
BNX 1010	168	144/500	2
BHT	64	40/67	4
GSPE	88.5	64.5/269	3
Quercetin	296	272/1133	1
TBHQ	33	9/38	6
Vitamin C	29	5/21	7
Vitamin E	60	36/50	5

Note: OIT for pure UHMWPE was 24 min.

$$\text{Net Effect of OIT(min)} = \text{OIT} - 24$$

$$\text{Net Effect (\%)} = [(\text{OIT}-24)/24]*100$$

4.2 Effects of Various Antioxidants on Durometer Hardness of UHMWPE

In order to understand the change in mechanical properties and the polymeric structure, hardness testing was performed on UHMWPE with 0.6 percent antioxidant concentrations. Table 3 indicates the effect of 0.6 percent antioxidants on Durometer

hardness of UHMWPE. It was observed that the addition of the antioxidant BHT to UHMWPE reduced the Durometer hardness of the polymer. The Durometer hardness number of UHMWPE with other antioxidants also seemed slightly lower than the pure polymer. However, the decrease in hardness may not be statistically significant. At least, it can be concluded that the addition of antioxidants did not increase the Durometer hardness of UHMWPE.

Table 3

Average Durometer Hardness at 1 Second

Antioxidant	Concentration	
	0.0%	0.6%
BHT	71.3	62.5
BNX 1010	71.3	68.9
GSPE	71.3	69.6
Quercetin	71.3	69.0
Vitamin E	71.3	69.5

Comparative hardness testing of polymers is often conducted to determine the level of cross-linking among polymeric chains. If additional cross-linking existed in specimens containing antioxidants, the hardness of the polymer would increase. From Table 3, it was observed that the addition of antioxidants did not increase the hardness of UHMWPE. Thus, it is concluded that the addition of antioxidants did not cause any significant cross-linking to this polymer.

4.3 Effects of Various Antioxidants on the Thermal Behavior of UHMWPE

The structural change in a polymer is related to its thermal properties such as melting temperature, on-set melting temperature, and heat of fusion (enthalpy). In general, melting temperature will increase with the development of any branching or cross-linking, or if the molecular weight of the polymer has increased. A decrease in on-set melt temperature could be related to a more diverse distribution of molecular chain length. An increase in enthalpy is related to an increase in crystallinity of the polymer. To evaluate the thermal behavior of UHMWPE with and without antioxidants, regular differential scanning calorimetry (DSC) was performed with a scanning rate of 10°C/min, from room temperature to 200°C, with a nitrogen flow of 50 mL/min.

Figure 3 illustrates the melting endothermal and the oxidation exothermal curve of one of the polyethylene samples. Heat flow (ΔH) is shown on the vertical axis and the temperature level (ΔT) on the horizontal axis. This graph illustrates an endothermic response signaled by a drop, and an exothermal response signaled by a rise in the curve.

Table 4 displays the effects of antioxidants on the thermal behavior of UHMWPE, which were determined by regular DSC. The crystallinity of UHMWPE with antioxidant was calculated by dividing the enthalpy by 290 J/g a crystallinity constant of 100 percent crystalline polyethylene. The DSC results show very little variation among the on-set melting temperatures of UHMWPE with various antioxidants. This fact

Sample: BNX 1010 0.6%
Size: 3.0000 mg
Method: HIGH TEMP REGULAR DSC
Comment: HIGH TEMP REGULAR DSC

DSC

File: CS-BNX0.1
Operator: CLIFF
Run Date: 10-Apr-00 11:06

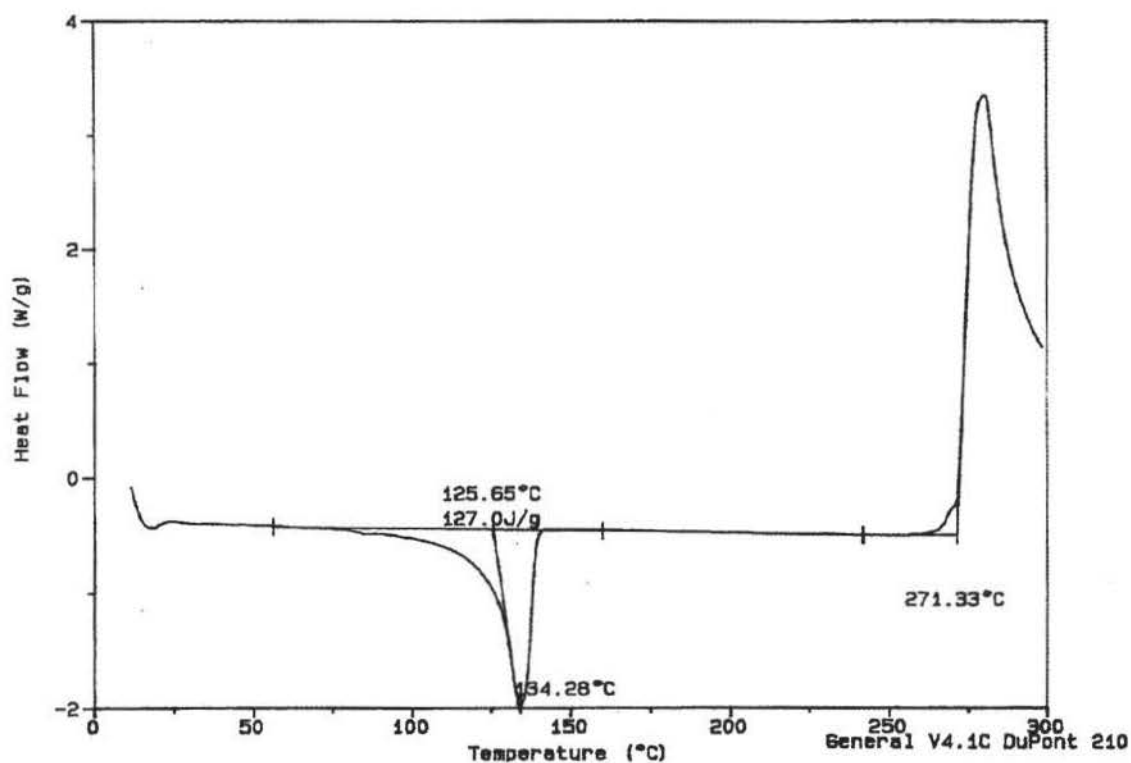


Figure 3 Regular Differential Scanning Calorimeter (DSC) graph showing both endothermal and exothermal curves

suggests that the distribution of the molecular chain length of UHMWPE was not altered significantly by addition of antioxidants. On the other hand, the melt temperature of UHMWPE with addition of quercetin and vitamin E was slightly higher than that of pure polymer. This could suggest the development of minor branching in the polymeric chain due to the incorporation of the two antioxidants. The heat of fusion and crystallinity of UHMWPE with quercetin and vitamin E were also reduced when the same two antioxidants were added. It is postulated that the decrease in crystallinity was related to slight branching of polymeric chains evidenced by increase in melting temperature, which was caused by the antioxidants.

Table 4

Differential Scanning Calorimeter (DSC) Results of UHMWPE with 0.6 Percent Antioxidant

Antioxidant	Melt Onset Temp (°C)	Melt Peak Temp (°C)	Enthalpy (J/g)	Crystallinity (%)
UHMWPE	128.77	136.28	164.6	56.8
BHT	128.79	136.16	167.2	57.6
GSPE	128.90	136.12	167.7	57.5
Quercetin	128.85	137.04	161.7	55.8
Vitamin E	129.1	137.27	146.9	50.7

Note. Crystallinity (%) = $[(J/g)/290]*100$

Table 5 illustrates the effects of antioxidants upon the oxidization temperature of UHMWPE. These tests were also performed with a regular DSC. The test parameters were changed to a maximum temperature of 300°C and the specimens were placed in open pans in an atmosphere environment.

The data in Table 5 indicate that quercetin was the most effective antioxidant at raising the oxidization temperature. UHMWPE with 0.6% quercetin had an oxidization temperature of 282°C, which represents an increase of 31°C or 34 percent above that of pure polymer. Other antioxidants also demonstrated very similar effectiveness at raising the oxidization temperature as they did in OIT testing with the exception of vitamin E, which moved up two positions in the ranking. The effectiveness of the studied antioxidants at a concentration of 0.6 percent could be arranged in descending order as follows: quercetin > BNX 1010 > vitamin E > GSPE > BHT > TBHQ > vitamin C.

Table 5

Oxidization Temperatures of UHMWPE with 0.6 Percent Antioxidant

Antioxidant	Oxidization Temp (°C)	Net effect of Antioxidant on Oxidization Temp (°C)/%	Ranking
Pure UHMWPE	211	None	
BNX 1010	271	60/28	2
BHT	237	26/12	5
GSPE	249	38/18	4
Quercetin	282	71/34	1
TBHQ	233	22/10	6
Vitamin C	230	19/9	7
Vitamin E	256	45/21	3

4.4 Effect of Antioxidant Concentration on OIT of UHMWPE

The next step in this study was to determine the effectiveness of the remaining six antioxidants as a function of concentrations. Identical test parameters were used throughout this study to determine OIT effectiveness.

Table 6 illustrates the results on OIT of UHMWPE with various antioxidants, at concentrations of 0.1, 0.2, 0.4, and 0.6 percent. The OIT of pure UHMWPE was 24 min. The net percent of OIT effectiveness was calculated by subtracting 24 min. from the OIT, dividing the remainder by 24, and multiplying that quotient by 100.

β -carotene was not tested at lower concentrations due to its pro-oxidant behavior at 0.6 percent. BNX 1010 was not tested due to its being an industrial antioxidant that

was used as a control at 0.6 percent. TBHQ and vitamin C were not tested at 0.1%, because they demonstrated little effectiveness at 0.2%.

Table 6

OIT of UHMWPE with 0.1, 0.2, 0.4, and 0.6 Percent Antioxidants (OIT [min]/Net Percent)

Antioxidant	Concentration			
	0.1%	0.2%	0.4%	0.6%
β-carotene	NA	NA	NA	18.5/-23
BHT	48/100	58/142	59/146	64/167
BNX 1010	NA	NA	NA	168/600
GSPE	49/104	58/142	86/258	89/271
Quercetin	191/696	227/846	269/1021	296/1133
TBHQ	NA	28/17	34/42	33/38
Vitamin C	NA	26/8	27/13	29/21
Vitamin E	43/79	49/104	52/117	60/150

Note. OIT of pure UHMWPE was 24 min. Net Percent = $[(\text{OIT}-24)/24]*100$.

Figure 4 depicts the OIT (min) of UHMWPE with antioxidants as a function of antioxidant concentration. All antioxidants showed positive effect on the OIT. However, their effectiveness was drastically different. Vitamin C had the least effect on increasing OIT of UHMWPE, which increased from 26 min. at 0.2 percent to 29 min. at 0.6 percent. The most effective of all antioxidants was quercetin, which had an OIT of 191 min. at 0.1

percent, a 696 percent increase from pure UHMWPE. Its OIT continued increasing to 296 min. at 0.6 percent, an increase of 1133 percent from pure UHMWPE. Among the six antioxidants studied, their effectiveness can be arranged in descending order as follows: quercetin > GSPE > BHT > vitamin E > TBHQ > vitamin C. The order is the same as that of 0.6 percent antioxidants.

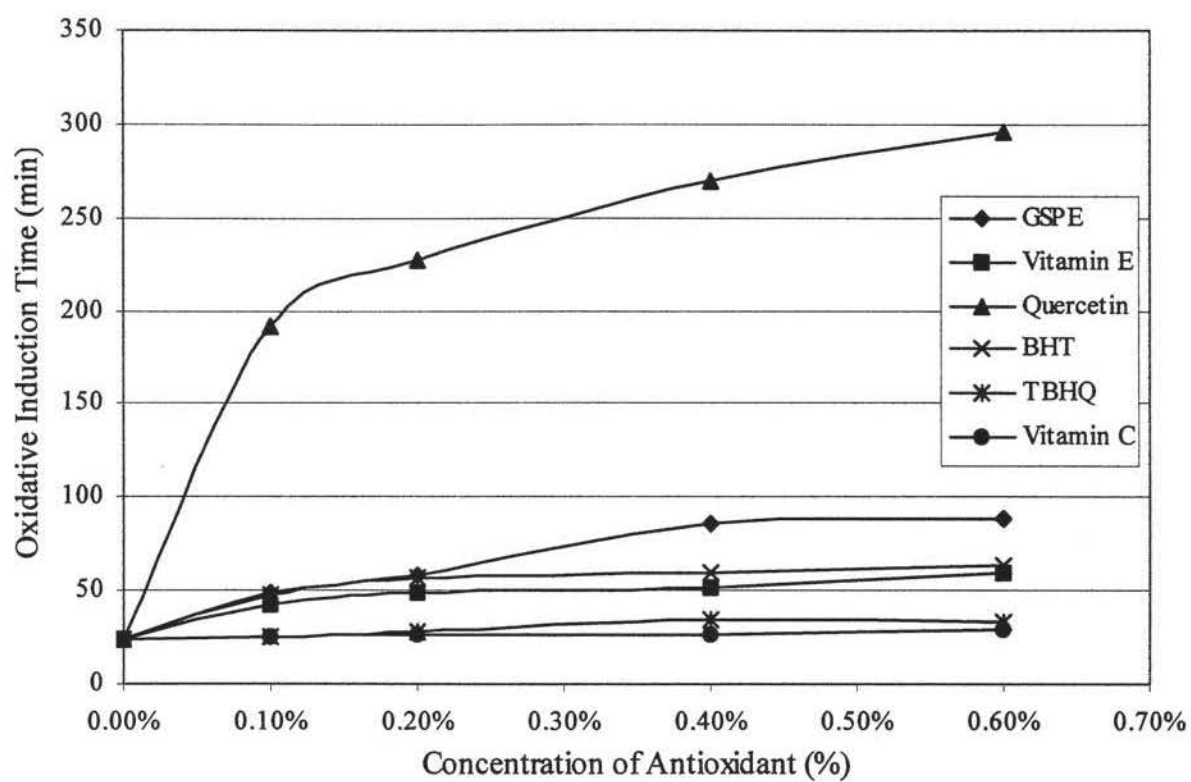


Figure 4 Oxidative induction time response to antioxidant concentrations

4.5 Effects of Antioxidant Concentrations on Hardness of UHMWPE

As previously stated, comparative hardness testing was used to determine the level of cross-linking between polymer chains, with additional cross-linking indicated by an increase in hardness. According to Table 7, it can be determined that the hardness of the polymer with BHT, quercetin, and vitamin E did not demonstrate a consistent correlation to concentration. This may indicate that variations in the cooling rate and pressures of the compression molding process may have a greater effect on hardness than the addition of antioxidants. The results do, however, indicate that the addition of antioxidants at lower concentrations does not increase the hardness of pure UHMWPE.

Table 7

Average Durometer Hardness at 1 Second as a Function of Antioxidant Concentrations

Antioxidant	Concentration				
	0.0%	0.1%	0.2%	0.4%	0.6%
BHT	71.3	61.5	66.2	66.8	62.5
GSPE	71.3	68.5	69.1	69.1	69.6
Quercetin	71.3	66.6	68.5	69.2	69.0
Vitamin E	71.3	67.4	65.6	69.0	69.5

4.6 Effects of Antioxidant Concentrations on the Thermal Behavior of UHMWPE

DSC results of Table 8 indicate the effect the addition of various concentrations of antioxidants had on thermal behavior of UHMWPE. The DSC results indicated very little variation in melt temperatures or melt on-set temperatures. There is also little or no correlation between variations in these temperatures and the antioxidant concentrations. This would suggest that the addition of antioxidants, at the concentrations studied, had little effect on the molecular structure of UHMWPE.

There is no consistent correlation between enthalpy or crystallinity and antioxidant concentrations. Since heat of fusion is related to many factors such as sample mass, shape, and contact with sample pans, the observed fluctuations in heat of fusion and crystallinity may be due to those experimental variations.

Table 8

Differential Scanning Calorimeter (DSC) Results

Antioxidant Concentration	Melt Onset Temp. (°C)	Melt Peak Temp. (°C)	Enthalpy (J/g)	Crystallinity (%)
Pure UHMWPE	128.77	136.28	164.6	56.8
BHT 0.1%	128.64	136.63	158.9	54.8
BHT 0.2%	128.96	136.14	155.1	53.4
BHT 0.4%	128.34	136.01	172.8	59.6
BHT 0.6%	128.79	136.16	167.2	57.6
GSPE 0.1%	128.99	136.70	157.0	54.1
GSPE 0.2%	128.71	136.21	156.2	53.9
GSPE 0.4%	128.59	136.06	166.7	57.5
GSPE 0.6%	128.90	136.12	167.7	57.6
Quercetin 0.1%	129.04	136.06	134.8	46.5
Quercetin 0.2%	128.96	136.15	147.1	50.7
Quercetin 0.4%	128.92	136.01	161.9	55.8
Quercetin 0.6%	128.85	137.04	161.7	55.8
Vitamin E 0.1%	128.73	136.26	159.5	55.0
Vitamin E 0.2%	128.60	135.78	171.9	59.3
Vitamin E 0.4%	128.58	135.69	161.7	55.8
Vitamin E 0.6%	129.16	137.27	146.9	50.7

4.7 Testing for Synergy Between Antioxidants

Research has shown that some antioxidants when used in combination can have a cooperative or increased level of effectiveness than when used individually. This cooperative or synergistic effect could be exploited to increase the OIT resistance of UHMWPE or to decrease antioxidant concentrations. Decreasing the antioxidant concentration could have two benefits. First, it would decrease antioxidant cost. Secondly, by utilizing lower concentrations any negative effects to the mechanical properties of UHMWPE that may result from the addition of antioxidants could be decreased.

To test for synergy, the four most effective antioxidants were mixed in all possible combinations, with individual antioxidant concentrations of 0.2 percent. OIT testing was performed for the synergy study.

Table 9 illustrates the experimental data and analysis to reveal any synergy between antioxidants. The first antioxidant in any combination was designated as “A”, whereas the second was “B”. “Net Actual Combination” represents the net increase in OIT of UHMWPE with the two antioxidants added. Net “A” only illustrates the net increase in OIT when only antioxidant “A” was added in the polymer. The data for net “A” only and net “B” only were based upon the results in Table 5. “Net Linear Projection” is predicted OIT (min), based upon possible contributions from both antioxidants when they were added individually. Taking BHT 0.2 percent and vitamin E 0.2 percent for example, the net increase in OIT was 34 min. when only 0.2 percent BHT was added and the net increase in OIT was 25 min. when only 0.2 percent of vitamin E

was added. Adding the contributions of 0.2 percent BHT and 0.2 percent vitamin E would result in a “Net Linear Projection” of 59 minutes.

Table 9

OIT of UHMWPE with Combinations and Individual Antioxidants at 0.2 Percent

Antioxidant Combination	Net Actual Combination (min)	Net “A” Only (min)	Net “B” Only (min)	Net Linear Projection (min)	Net Synergy (min/%)
BHT 0.2% (A) Vitamin E 0.2% (B)	62	34	25	59	3/5
BHT 0.2% (A) GSPE 0.2% (B)	65	34	34	68	-3/-5
BHT 0.2% (A) Quercetin 0.2% (B)	127	34	203	237	-110/-46
GSPE 0.2% (A) Quercetin 0.2% (B)	298	34	203	237	61/26
GSPE 0.2% (A) Vitamin E 0.2% (B)	51	34	25	59	-8/-14
Quercetin 0.2% (A) Vitamin E 0.2% (B)	149	203	25	228	-79/-35

Note. OIT for pure UHMWPE was 24 min.

Net Actual Combination = OIT Combination – 24.

Net “A” or “B” = Individual OIT – 24.

Net Linear Projection = Net “A” + Net “B”.

Net Synergy (min) = Net Actual Combination – Net Linear Projection.

Net Synergy (%) = (Net Synergy (min)/Net Linear Projection)*100.

“Net Synergy” is the difference in OIT (min) between “Net Actual Combination” and “Net Linear Projection”. If there is neither synergy or canceling effect between the two antioxidants, the “Net Synergy” would be zero. If there is any synergy between the

two antioxidants, the “Net Synergy” will be positive. Negative “Net Synergy” means that one antioxidant cancels benefits to OIT from another antioxidant. “Net Synergy (min)” is expressed in terms of OIT minutes, whereas, “Net Synergy (%)” is calculated relative to the linear projected OIT.

The results indicate that two of the six combinations of antioxidants demonstrated a cooperative synergy. The combination of BHT/Vitamin E demonstrated a slight synergy with an increase of 3 minutes in OIT or 5 percent increase in OIT effectiveness, over the individual contribution from each antioxidant. The strongest synergy was demonstrated by the GSPE/Quercetin combination. This combination of antioxidants had an increased OIT of 61 minutes, which resulted in a 26 percent increase of effectiveness. The other four combinations demonstrated no synergy effects and in some cases their effect on OIT were far below their individual effectiveness. The results of this research indicate that there is a synergy between some antioxidant combinations and that further research may be warranted to determine optimum concentrations.

4.8 Effects of Antioxidant Combinations on Hardness

To evaluate any change in mechanical properties and materials structure, hardness testing was performed on the UHMWPE/antioxidant combinations that demonstrated synergy in OIT effectiveness. From Table 10, it can be determined that the addition of antioxidant combinations did not increase the Durometer hardness of the polymer. It can then be concluded that the addition of antioxidant combinations to UHMWPE does not cause any significant cross-linking.

Table 10

Average Durometer Hardness at 1 Second of Samples with Antioxidant Combinations

Antioxidants	Pure UHMWPE	Combination	“A” Only	“B” Only
BHT 0.2%	71.3	67.2	66.2	69.0
Vitamin E 0.2%				
GSPE 0.2%	71.3	69.2	69.1	68.5
Quercetin 0.2%				

4.9 Effects of Antioxidant Combinations on the Thermal Behavior of UHMWPE

Table 11 illustrates the effect of antioxidant combinations on the thermal behavior of UHMWPE, as determined by regular DSC. The results show very little variation in the melt and melt on-set temperatures, which suggests that the molecular chain length and degree of cross-linking were not affected by the addition of antioxidant combinations at this concentration. The enthalpy or percent crystallinity of GSPE/quercetin combination was somewhat higher than the other specimens tested, which may indicate an ordering of the amorphous structure into a more crystalline one.

Table 11

Differential Scanning Calorimeter (DSC) Results of UHMWPE with Combinations of Antioxidants

Antioxidants	Melt Onset Temp (°C)	Melt Peak Temp (°C)	Enthalpy (J/g)	Crystallinity (%)
UHMWPE	128.77	136.28	164.6	56.8
BHT 0.2% & Vitamin E 0.2%	128.78	136.23	164.6	56.8
GSPE 0.2% & Quercetin 0.2%	128.86	136.10	195.4	67.4

Note. Crystallinity (%) = $[(J/g)/290]*100$

CHAPTER V

Conclusion

The following conclusions were made based upon the experimental effects of antioxidants on the oxidative induction time (OIT), Durometer hardness, thermal behavior, and thermal stability of ultra high molecular weight polyethylene (UHMWPE).

1. The oxidative induction time (OIT) of ultra high molecular weight polyethylene (UHMWPE) was increased with the addition of antioxidants.
2. The OIT of UHMWPE was increased by over 1100 percent with the addition of 0.6 percent quercetin.
3. β -carotene acted as a pro-oxidant when combined with UHMWPE.
4. The effectiveness of antioxidants on OIT in descending order was as follows: quercetin > BNX 1010 > GSPE > BHT > vitamin E > TBHQ > vitamin C > β -carotene.
5. Oxidative induction times increased as antioxidant concentrations were increased within the concentrations studied.
6. There is a weak synergy between BHT and vitamin E and a strong synergy between GSPE and quercetin.
7. Durometer hardness of UHMWPE is not greatly affected by the addition of antioxidants, either individually or in combination.
8. Thermal behavior of UHMWPE was not greatly affected by the addition of antioxidants, either individually or in combination.
9. Thermal stability of UHMWPE was increased with the addition of antioxidants.

Recommendation for Further Research

1. Research the synergy between BHT/vitamin E and quercetin/GSPE to determine the most effective concentrations.
2. Research the effectiveness of the antioxidants used in this study on post irradiation OIT, thermal properties, and mechanical performance of UHMWPE.
3. Research the effects of antioxidants on post irradiated UHMWPE to determine wear rate and particulate generation.
4. Research the effects of cooling on the development of crystalline structure in UHMWPE.
5. Research the effectiveness of antioxidants used in this study at concentrations greater than 0.6 percent on OIT, thermal properties, and mechanical performance of UHMWPE.

References

American Society for Testing and Materials (1994), Standard Test Method for Rubber Property-Durometer Hardness. D 2240-9.

Bagchi, D., Garg, A., Krohn, R. L., & Bagchi, M. (1997). Oxygen Free Radical Scavenging Abilities of Vitamins C and E, and a Grape Seed Proanthocyanidin Extract *In Vitro*. Research Communications in Molecular Pathology and Pharmacology, 95, (2), 179-189.

Balavoine, G. G. A. & Geletii, Y. V. (1999). Peroxynitrite Scavenging by Different Antioxidants. Part 1: Convenient Assay. Biology and Chemistry, 3, (1), 40-54.

Blaine, R. L., Lundgren, C. J., & Harris, M. B., (1997). Oxidative Induction Time – A Review of DSC Experimental Effects. Oxidative Behavior of Materials by Thermal Analytical Techniques, ASTM STP 1326, A. T. Riga and G. H. Paterson, (Eds.), American Society for Testing and Materials.

Cadenas, C., & Packer, L. (1996). Handbook of Antioxidants. New York, New York: Marcel Dekker, Inc.

Chen, X., & Ahn, D. U. (1998). Antioxidant Activities of Six Natural Phenolics Against Lipid Oxidation Induced by Fe^{2+} of Ultraviolet Light. Journal of the American Chemists Society, 75, (12), 1717-21.

Costa, L., Luda, M. P., Trossarelli, L., Brach del Prever, E. M., Crova, M., & Gallinaro, P., (1998). Oxidation in Orthopedic UHMWPE Sterilized by Gamma-Radiation and Ethylene Oxide. Biomaterials, 19, 659-668.

Dougherty, M. E. (1993). Effectiveness of Natural Antioxidants Compared to Synthetic Antioxidants. International Food Ingredients, (3).

Foreman, J. A., Lundgren, C. J., & Gill, P. S. (n. d.). Measurement of the Physical Properties of Engineering Thermoplastics Using Thermal Analysis. TA Instruments Publication, TA-090.

Goldman, M., Lee, M., Gronsky, R. & Pruitt, L. (1996, May 15). Oxidation of Ultrahigh Molecular Weight Polyethylene Characterized by Fourier Infrared Spectrometry. Journal of Biomedical Materials Research, 37, (1), 43-50.

Hall, C. & Cuppet, S. (1993, May). The Effects of Bleached and Unbleached Rosemary Oleoresins on Light-Sensitized Oxidation of Soybean Oil. Journal of American Oil Chemists Society, 70, 477-482.

Han, D., Yi, O., & Shin, H. (1991, October). Solubilization of Vitamin C in Fish Oil and Synergistic Effect with Vitamin E in Retarding Oxidation. Journal of American Oil Chemists Society, 68, 740-743.

Henry, L. K., Catignani, G. I., & Schwartz, S. J. (1998, October). The Influence of Carotenoids and Tocopherols on the Stability of Safflower Seed Oil During Heat-Catalyzed Oxidation. Journal of the American Oil Chemists Society, 75, (10), 1399-1402.

Jiyun, L., Tai, Z., & Hopkins, S. J. (1997). Quercetin. Cardioprotectant, Antineoplastic, Antioxidant. Drugs of the Future, 22, (7), 720-24.

Mayzo, Inc. (1994). BNX 1010/1010G/1010E. Product Information Brochure, Norcross, GA.

McCullen, Geoffrey, & Miller, R. (1998). Hip and Knee Replacement: A Patients Guide. The Consumer Health Information Source Book, 1, 151-58.

Nolan, J. F. & Phillips, H. (1996, September 28). Joint Replacement and Particulate Wear Debris. Lancet, 348, (9031), 839-840.

Papas, A. M. (1999). Antioxidant Status, Diet, Nutrition, and Health. Boca Raton, Florida: CRC Press LLC.

Premnath, V., Harris, W. H., Jasty, M. & Merrill, E. W. (1996, September 1). Gamma Sterilization of UHMWPE Articulator Implants: An Analysis of the Oxidation Problem. Biomaterials, 17, 1741-1753.

Ray, S. D., Kumar, M. A., & Bagchi, D. (1999, September 1). A Novel Proanthocyanidin IH636 Grape Seed Extract Increases in Vivo B_{cl}-X_L E Expression and Prevents Acetaminophen-Induced Programmed and Unprogrammed Cell Death in Mouse Liver. Archives of Biochemistry and Biophysics, 369, (1), 42-58.

Strong, A. B. (1996). Plastics: Materials and Processing. New Jersey: Prentice-Hall, Inc.

Tomita, N., Kitakura, T., Onmori, N., Ikada, Y., & Aoyama, E. (1999) Prevention of Fatigue Cracks in Ultrahigh Molecular Weight Polyethylene Joint Components by the Addition of Vitamin E. Journal Biomedical Material Research, 48, (4), 474-78.

Young, T. H., Cheng, C. K., Lee, Y. M., Chen, L. Y. & Huang, C. H. (1998). Analysis of Ultrahigh Molecular Weight Polyethylene Failure in Artificial Knee Joints: Thermal Effect on Long-Term Performance. Journal of Biomedical Materials Research, 48, (2), 159-164.