ABSTRACT

DEVELOPMENT OF A GEL CONTENT ANALYSIS PROTOCOL FOR ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

by
Max H. Jeanty

A modified procedure based upon ASTM (D 2765 - 90) to determine the gel content of crosslinked polyethylene plastics was developed. The new procedure was applied to ram extruded Ultra High Molecular Weight (UHMWPE) implant components processed under different manufacturing conditions. This new evaluation tool provides consistent results with greater accuracy and consistency compared to the American Society for the Testing of Materials (ASTM) method. Using the same tool, several relationships between the UHMWPE processing conditions and gel content were established. The amount of gel content is related to the crosslinked material. It has been shown that the more crosslinking present in a material, the better its resistance is to wear. This new development is very useful in the comparison of various UHMWPE raw materials and the development of new UHMWPE materials.

DEVELOPMENT OF A GEL CONTENT ANALYSIS PROTOCOL FOR ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

by
Max Harold Jeanty

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Biomedical Engineering

Biomedical Engineering Committee

October 1996

APPROVAL PAGE

DEVELOPMENT OF A GEL CONTENT ANALYSIS PROTOCOL FOR ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

Max H. Jeanty

Dr. Raj Sodhi, Thesis Advisor	Date
Associate Professor, Department of Mechanical Engineering, NJIT

Dr.D.C. Sun, Committee Member	Date
Manager - Polymer Technology Laboratory
Howmedica Inc.,Worldwide R&D

Dr. David Kristol, Committee Member	Date
Associate Professor, Department of Biomedical Engineering, NJIT

BIOGRAPHICAL SKETCH

Author:	Max H. Jeanty
Degree:	Master of Science in Biomedical Engineering
Date:	October 1996

Undergraduate and Graduate Education:

- Master of Science in Biomedical Engineering
  New Jersey Institute of Technology,
  Newark, New Jersey, 1996

- Bachelor of Art in Physics
  Rutgers The State University of New Jersey
  Newark, New Jersey, 1993

Major: Biomedical Engineering

Thanks and Praise to the Lord for making me.
Thanks to my parents (Philippe and Melila) for believing in education.

ACKNOWLEDGMENT

I wish to express my sincere gratitude to Dr. Raj Sodhi, Dr. D.C. Sun, Dr. Shi-Shen Yau, Gregg Schmidig, and Howmedica Inc. for their help in completing this thesis.

I also want to express my immense gratefulness and thanks to Dr. Ronald Kane and Dr. David Kristol for their support, understanding, great trust, and friendship to me.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

Chapter **Page**

LIST OF TABLES

Table **Page**

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Objectives

It has been shown that increase in wear resistance is correlated with the amount of crosslinking in biomaterials[31]. The higher the wear resistance, the better the implant performs in the body. For engineers looking to improve the physical and mechanical properties of Ultra High Molecular Weight Polyethylene (UHMWPE), a standard tool for measuring the amount of crosslinking is a necessity. By using such a tool for crosslinking analysis of various materials produced under different processing conditions, it will be possible to predict or confirm that wear resistance, fatigue, and other mechanical properties are improved.

Although there exists an ASTM (The American Society for the Testing of Materials) standard for the determination of gel content in crosslinked ethylene plastics, the method however is inappropriate for UHMWPE without substantial modification. On the other hand, the polymer wear is regarded as the major issue for long term success in total joint replacement. Manufacturers are making process improvements UHMWPE material properties. Therefore the objectives of this study were:

(1) To improve the ASTM standard test method for the determination of gel content for crosslinked ethylene plastics and utilize the modified procedure for measurements of gel content in UHMWPE implant components.

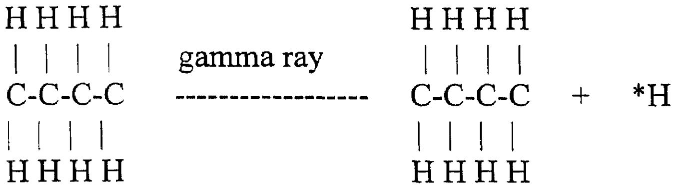
(2) To study the relationship between gel content and the manufacturing process conditions of UHMWPE implants.

1.2 Crosslinking Overview

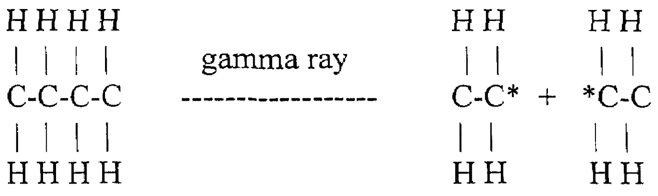
Not too long ago, polymer engineers at Howmedica Worldwide Inc. discovered two major structural changes induced in UHMWPE implants upon radiation stabilization which is the exposure of a material to ionizing radiation in order to destroy micro-organisms. These were chain scission through oxidation and crosslinking. The latter is believed to be a good indication for material property improvements in UHMWPE.

This process is at the center of the modified test method developed. Once the material is crosslinked, dissolution is very difficult due to the chemical bonds created. The amount of gel residue in the extraction is a good indication for possible crosslinked elements. The gel itself is the focus of our investigation in the extraction process.

As mentioned before, crosslinking occurs as a result of radiation. When UHMWPE is subjected to gamma-ray radiation, breakage of carbon-hydrogen (C-H) or carbon-carbon covalent bonds occurs:



$$\begin{array}{c} H\;H\;H\;H \\ |\;\;|\;\;|\;\;| \\ C{-}C{-}C{-}C \\ |\;\;|\;\;|\;\;| \\ H\;H\;H\;H \end{array} \quad \overset{\text{gamma ray}}{\text{------------------}} \quad \begin{array}{c} H\;H\;H\;H \\ |\;\;|\;\;|\;\;| \\ C{-}C{-}C{-}C \\ |\;\;|\;\;|\;\;| \\ H\;H\;H\;H \end{array} \quad + \quad {}^{*}H \qquad (1)$$



$$\mathrm{C\text{-}C\text{-}C\text{-}C} \xrightarrow{\text{gamma ray}} \mathrm{C\text{-}C^{*}} + \mathrm{{}^{*}C\text{-}C} \qquad (2)$$

Literature reports indicate that the side group cleavage (C-H, equation (1)) rather than the backbone scission (C-C, equation (2)) is the dominant reaction for PE [1]. However, the formation of free radicals (carbon atoms containing an unpaired electron) in equation (1) can initiate a series of oxidation reactions if oxygen is present. Inter- and intra-molecular crosslinking can also occur; in the presence of oxygen, crosslinking is reduced. Each reaction mechanism as described in the literature [2] is briefly discussed below.

Formation of free radicals

Formation of free radicals occurs in UHMWPE upon radiation. The amount of free radicals is dependent on the radiation dose and independent of radiation environment..

$$\text{Polyethylene (PH)} \xrightarrow{\text{gamma ray}} \text{r. (free radicals)}$$

Radiation in the presence of air

(1) Formation and propagation of peroxides and hydroperoxides.

$$\text{r.} \longrightarrow \text{rO}_2\text{.} \quad \text{(peroxide free radicals)}$$

rO2. + polyethylene (PH) ---------------- rOOH + P.

P. + O2 ------------------ PO2. (new peroxides)

(2) End products of oxidation reactions

ro2. or po2. + polyethylene (PH) --------------- -R2C=O (ketones), RCH2OR (esters), RHC=O (aldehydes), R(OH) C=O (carboxyl acids), and other oxygen containing species.

(3) crosslinking reactions

2 r. ----------- R-R (carbon-carbon crosslinks)

r. + rO2. ----------- ROOR (peroxide crsslinks)

(4) Peroxides breakdown at room and elevated temperatures

room or elevated temperature

rOOH -------------------------------------- rO. + OO. (new free radicals)

rO. or OH. + O2 ----------------------- oxidation products

From the above, when radiation is carried out in the presence of air, oxidation reactions between free radicals and oxygen that occur in some parts of polymer result in side group formation (ketones), the incorporation of oxygen in the main chain (esters) or broken chains reducing the molecular weight (aldehydes and acids). At the same time, free radicals react with each other in other parts of the polymer to form chemical crosslinks which increase molecular weight. During post-radiation shelf storage, oxidation becomes the dominant reaction causing a gradual reduction in molecular weight with changes to material properties.

UHMWPE is a high density polyethylene with a very high degree of polymerization. Its molecular weight measured by the light scattering method is in the region of 3.5 to 4 million. This value represents what is generally known as the "weight average molecular weight". Other methods of determination may give results which deviate to a greater or lesser degree from this value.

The high molecular weight gives rise to high solution viscosity and to pronounced viscoelastic behavior of the melt. As the molecular weight of polyethylene increases, higher values are obtained for a number of technically important properties including notched impact strength, energy absorption capacity at high loading rates, ultimate tensile strength at elevated temperature and also resistance to stress cracking. Therefore its high molecular weight makes UHMWPE suitable for all applications where lower molecular weight grades do not meet the requirements.

UHMWPE has been extensively used, treated, and modified since its general acceptance for the manufacture of biological replacement parts in human. Their degrees of success varies[3]. Tibial knee arthroplastics, patella arthroplastics and molded acetabular cups all contain UHMWPE as their main structure element. The treatments and modification that it has been subjected to are the only ways available to the research engineer to better its general mechanical and physical properties. The work that this thesis study has been involved in for the past months and that Howmedica Research and Development has been committed to for the past 10 years have had UHMWPE at its central point. By using diverse methods and procedures, we keep on stretching the properties of UHMWPE making it stronger, more stable, and more durable than any of the competitors.

There has been some concerns related to fatigue and wear of the plastics which have limited the long term success of total joint replacements. Used as the bearing material in total hip and knee replacement, it is usually one of the first element in the reconstruction components to fail because of the wear between the metal components and the polyethylene which is also dependent on the patient conditions.

The more crosslinking present in a processed material, the better the chemical, the mechanical, and physical properties of that material. The crosslinked material is directly related to the change in mechanical properties of the plastic. A crosslinked material is believed to have better wear resistance, higher ultimate tensile and impact strength, better creep resistance, and many other necessary properties for body implant materials. Therefore, we have to have a tool that will allow us to find out whether or not a material is likely to be crosslinked and if possible how much of it is crosslinked.

1.3 Gel Content Overview

The standard method for the determination of gel content of crosslinked ethylene plastics is published by ASTM and is briefly presented below (See the ASTM standard book for the complete procedure). This method of determination has been widely used for low density polyethylene. It can also be used for the extraction of UHMWPE although it is warned that there were reports that at times, it did not completely dissolve the materials. Therefore, this procedure was used in order to measure the gel content of our processed plastics. The procedure consists of:

1. Preparation of a specimen holder (stainless steel wire cloth) of a fixed dimension.
2. Use of a fixed weight of the ground and screened sample in a cage which is stapled shut.
3. Use of a fixed amount of solvent in a 2000 ml flask.
4. Extraction of the specimen for a specified time.
5. Drying of the specimen in a vacuum oven.
6. Cooling and weighing of the extracted compound.

This procedure was originally designed for low density PE plastics, but it was also said that it could be used for UHMWPE. Due to the many inconsistencies repeatedly occurring, we realized that the procedure had a lot of limitation when used for UHMWPE. There was room for improvement in many elements in the procedure. The most critical items were:

- The samples weight
- The wire mesh size

- The solvent concentration
- The procedure duration
- The drying method
- And the humidity control

One of the main reason for the inconsistencies have been attributed to the different chemical structure of low density Polyethylene as opposed to UHMWPE. All our observations support this fact and clearly confirm that the procedure needed to be modified and improved to better fit our use. Following is some of our most important observations:

(1) The sample preparation method used in the ASTM procedure is lengthy. Its main difficulty lie in the rigidity of the 120 US gage stainless steel wire. Being so rigid, it is difficult to form a cage that needs to be closed. A close observation of the cages after many early experiments tells us that as a result of the staples used, the cages were infected with holes that contributed to even more leakage of its content.

(2) The weight used is directly related to the volume of xylene in the flask. For a fixed amount of xylene (1.2 liter in ASTM), the more weight we used for the samples, the more difficult it is for it to dissolve the samples. This as a result gave inaccurate information about the gel content of the material as the chance of precipitation of the plastics is enhanced upon cooling. This in fact will cause the weight after extraction to be higher than the actual value, corresponding to total

crosslinking in the material. It is a problem to have such an interpretation of results which in this case is the wrong conclusion.

(3) Drying of the samples are usually done in vacuum oven overnight at 150 °C. To avoid oxidation and moisture absorption, the oven needed to be purged with nitrogen gas before and after placement of the samples. This process is lengthy and tedious. It had to be reduced for good engineering and industrial practice.

Therefore although it is mentioned that the procedure could be used for UHMWPE, it turned out based on all our observations, and the many inconsistencies in the result generated that it was inapplicable. On these premises, we set out to bring some improvements in the ASTM procedure.

1.4 Polyethylene

Before getting into the material and method used, we find it necessary to present some background information pertaining to the nature of polyethylene, its application in the biomedical field, and the mechanism involved in PE oxidation.

Polyethylene is produced by the polymerization of ethylene monomer. There are various processing methods used, which can greatly alter the characteristics of polyethylene. UHMWPE is manufactured by the Ziegler-Natta catalytic process at temperatures around 60 degrees Celsius and a low pressure of 3-10 atmospheres [4]. The incorporation of catalyst modifiers such as AlCl3 or BeF2 in polyethylene alters the amount of crystallites formed. Such control can produce a UHMWPE with varying physical properties. The catalyst modifier may produce polyethylene with superior strength but poor abrasive resistance (low crystallinity), or with improved chemical resistance to oxidation and abrasion (high crystallinity). UHMWPE implant components can be manufactured by:

(A) Compressing the feed stock powder into polyethylene blocks by using a hydraulic heated press geared to produce sheets from which the desired product can be shaped or formed by machining[5]. At present more than 60 percent of the UHMWPE is pressed into blocks with dimensions in the order of 2 meters to 8 meters lengths, widths of 1 meter to 2 meters and sheet thickness of 1 millimeter to 400 millimeters. The sintering time used to melt the powder stock in the mold is one hour for every 10 millimeters of plastic at a temperature of 200 degrees Celsius[5,6].

(B) Direct injection molding into a heated mold. The shapes possible are dependent on the die used, however, these shapes are limited due to the viscous nature of UHMWPE. In the molten state, products formed include solid rods, hollow rods and profiles[6].

(C) Ram extrusion of the powdered UHMWPE by a heated hydraulic ram makes it possible to produce continuous solid rods up to 300 mm in diameter[6]. The rods are machined to yield the desired product.

Semi-finished goods of UHMWPE are not molded under air exclusion [5,6]. Hence, processing of the polyethylene powder reduces the molecular weight of the polymer by up to 10%[7]. The reduction in molecular weight is due to thermal oxidative degradation during processing. This process may be reduced by using an inert gas[5].

For UHMWPE to be used as an implant material, it must have the following limits for residues [8]:

ash	<150 PPM
titanium	<20 PPM
aluminum	<40 PPM
calcium	<50 PPM
chlorine	<20 PPM
chromium	no traces

1.5 Biomedical Applications of Polyethylene

UHMWPE is currently the polymer most often used in orthopedic prostheses. Its primary application has been in the acetabular cup component for total hip arthroplasty, but it has also found extensive use as a bearing surface in the knee, ankle, shoulder, wrist prostheses, and as a prosthetic cruciate ligament[9-10]. This general use has resulted primarily from the good abrasion resistance and biocompatibility of UHMWPE. In spite of its relatively successful use in total hip replacements, a great deal of concern still exists about the use of polyethylene, particularly in other applications[11]. A desirable feature of a biomedical plastic generally is not subject to expansion due to water absorption[10-11].

1.6 Mechanism of Polyethylene Oxidation

Virgin UHMWPE material is hydrophobic and has very good resistance to aggressive media. However, upon gamma-ray sterilization, free radicals are generated in the UHMWPE. The oxidation reaction takes place between free radicals (molecules with unpaired electron) formed during irradiation, and oxygen (and/or other oxidants) found in air, in the body, or in the UHMWPE. After several years of post-irradiation aging in air, material property changes in UHMWPE resulting from this oxidation have been observed[13-14]. These include increases in modulus, tensile yield strength, crystallinity, and density ; and decreases in ultimate tensile strength, elongation, toughness, and molecular weight. In some reports, a subsurface white band has been observed in UHMWPE implants after a long period of post-irradiation aging[14,15]. Early brittle fractures of components initially implanted after long periods of shelf aging, e.g., eight years or more, have been anecdotally reported. A casual relationship between these events and shelf aging has not been established.

Howmedica Research and Development has conducted a thorough literature search and several research programs to better understand the oxidative reaction mechanism. Irradiation and post-irradiation effects are complex and not completely understood at this time. Further research is required to more fully define the precise changes in properties with time after radiation sterilization, and such work is ongoing.

However, from the studies to date, a sufficient understanding has emerged for the development of a process that virtually eliminates oxidation and also improves the material properties of UHMWPE.

As we can see, the presence of oxidation reduces the extent of crosslinking in a material and instead promotes chain scission and bond breakage responsible for the fractures and wear of the components.

CHAPTER 2

MATERIALS AND METHODS

RAM extruded UHMWPE rod made from GUR 415 resin were used throughout the study. Five types of UHMWPE(shown in the next table) were prepared for evaluation: Unirradiated, Irradiated at 2.5 Mrad in air, Inert irradiation (2.5 Mrad) followed by stabilization, processed at 500 degrees Fahrenheit and processed at 525 degrees Fahrenheit.

Table A UHMWPE Samples Analyzed

UHMWPE Sample	**Sterilization / Radiation Process**
Unirradiated	Extruded at around 460 °F; no radiation or other treatments
Air Irradiated	Extruded sample packed and irradiated in air at a dose of 2.9 Mrads
Stabilized	Extruded sample packed and irradiated in nitrogen at a dose of 2.9 Mrads followed by the stabilization process.
500 °F	Extruded sample at 500 °F; irradiated in nitrogen at a dose of 2.9 Mrads followed by the stabilization in nitrogen
525 °F	Extruded sample at 525 °F; no radiation but stabilization in nitrogen

2.1 Processing of UHMWPE

(The synthesis method of UHMWPE is presented in APPENDIX A)

Due to its high-melt viscosity, the molding and forming methods commonly used for processing thermoplastics cannot be applied to process UHMWPE. In order to overcome the high melt viscosity and viscoelasticity, the processing of UHMWPE requires a proper combination of temperature, high pressure, and time to achieve complete plastification. Currently, three processes have been developed to consolidate UHMWPE resin powder into useful shapes. In the compression molding process, sheets or blocks of various sizes are produced with a heated mold and press. In this case, a sufficient amount is poured into a mold, cold compacted, and then hot molded in a press.

Ram extrusion is essentially a continuous compression process. Rods and other shapes are produced by feeding UHMWPE powder into an electrically heated die (or mold), in which a plunger driven by an oil-hydraulic mechanism is moved backwards and forwards for compression. Following ram extrusion, the rods are annealed at a temperature slightly above the melting temperature of UHMWPE to improve material dimensional stability. Products, such as acetabular inserts, tibial inserts, or patellar inserts, are then machined to their final configurations from the compression molded blocks or ram extruded rods.

Depending on the temperature of extrusion, a UHMWPE can have different properties. UHMWPE can also be directly compression molded into final articles. However, special care must be taken to ensure uniform temperature and pressure during heating and cooling in order to achieve complete plastification. In general, this process is successful only with parts whose shape are axially symmetric.

We have used three types in this study:

Extrusion at 460 °F

This is the Poly Hi standard material. Poly Hi Solidur is an extruder located in Fort Wayne, Indiana. The material is extruded at around 460 °F. Its dwell time (duration time) in the die is approximately 90 minutes. It is then exposed to the ambient condition.

Extrusion at 500 °F

This type of UHMWPE is extruded at 500 °F. Its dwell time is around 140 minutes. The whole extrusion process is done in a nitrogen environment where the oxygen concentration in the system is below 170 PPM.

Extrusion at 525 °F

This type of UHMWPE is extruded at 525 °F. The whole extrusion process is done in a nitrogen environment where the oxygen concentration in the system is also below 170 PPM.

The manufacturing process conditions that we have used in this project were: air irradiation, duration stabilization. The following is a brief description of the irradiation processes.

2.2 Types of Irradiation Processes

The three types of reaction mechanisms that can occur during irradiation are presented below (A chart identifying the reactions is presented in APPENDIX B). Irradiation can be achieved in the presence of air or an inert atmosphere, or by the Duration Stabilization process. This figure gives a schematic comparison for the three processes.

A. Irradiation in the presence of air.

This case applies to UHMWPE components packaged in air prior to gamma irradiation. Free radicals produced by gamma irradiation (1a) will react with oxygen in the air and in the UHMWPE to initiate a series of oxidation reactions (1b), or react with each other to form a carbon-carbon chemical bond. The resultant structural changes include chain scission (1c), or crosslinking (1d). The oxidation can take place during irradiation, during shelf aging, or potentially, in vivo, but the latter to a lesser extent.

Specifically, the air irradiated rods used in this study, followed this process:

(1) The rod is packaged in air environment where the nominal oxygen concentration in the package is approximately 20.5%.

(2) Then it is sent for irradiation (nominal radiation dosage is around 2.9 Mrads)

B. Irradiation in an inert atmosphere.

This case applies to UHMWPE components packaged in an inert atmosphere (e.g., nitrogen, argon, or vacuum), prior to gamma irradiation. Since no oxygen is present during irradiation, some free radicals will combine with other neighboring free radicals, resulting in crosslinking (1d).

This reaction can continue after irradiation, but at a slow rate at room temperature. Uncombined free radicals are still present in UHMWPE even after several years of post irradiation aging[16]. During shelf storage, oxygen can leak into the package and react with uncombined free radicals to cause oxidation. Oxidation may also occur in vivo, although to lesser extent, between uncombined free radicals and oxidants (such as oxygen, hydrogen peroxide, and enzymes). Therefore, irradiation in an inert atmosphere can eliminate short-term oxidation, but cannot prevent oxidation in the long term.

Note:Rods irradiated in inert atmosphere were not used in this study.

C. Duration Stabilization process.

This new process consists of three steps, namely an initial packaging of UHMWPE in nitrogen, gamma irradiation, and the post-irradiation stabilization step. The first two steps serve to minimize oxidation during irradiation. In the third step, the irradiated package containing the UHMWPE component is stored in a precisely controlled environmental chamber at mildly elevated temperature (between body temperature and 60 °C) for a sufficient time to crosslink virtually all the reactive free radicals. A more detailed description of this process is given in US Patent No.5,414,049[20]. After the Duration Stabilization process is complete, evaluation shows negligible oxidation when the component is re-exposed to oxygen. Not only is oxidation (both short-term and long-term) substantially eliminated, but the increased crosslinking from the process also results in improved creep resistance and improvements in other material properties.

In the rods used, specifically the steps involved:

(1) The rod is packaged in air environment where the nominal oxygen concentration in the package is approximately 20.5%.

(2) Sent for irradiation (nominal radiation dosage is around 2.9 Mrads)

(3) Then Stabilization in an oven under nitrogen environment for 6 days at 50 °C

2.3 Samples Preparation

The samples consist of slices of UHMWPE that were microtomed to approximately 5 micron thick using a Reichert-Jung microtome machine. This was followed by step 1 and 2 in the modified procedure (section 2.5) for the majority of the experiments.

2.4 Description of ASTM Method

We used the standard method for determination of gel content of crosslinked ethylene plastics designed by ASTM (The American Society for the Testing of Materials- D 2765-90). The test method A (referee test method) was the most appropriate for the gel content determination of UHMWPE.

The main elements of the procedure follow.

- A specimen holder made from a US No. 120 stainless steel wire cloth (wire diameter is .085 millimeter) measuring 80 millimeters by 40 millimeters are to be folded and closed.
- About 300 milligram of sliced plastics is to be placed in the cages
- 1000 milligrams of materials in a 2000 milliliter flask is sufficient for the extraction with 10g of antioxidant (to prevent oxidation of UHMWPE which may cause its degradation)
- The extraction is to take place in enough solvent (xylene) for 12 hours.

Then the samples are to be dried in a vacuum oven preheated to 150 °C.It also suggests placing the samples afterward in a desiccator to avoid moisture absorption before weighing.

2.5 Description of Modified Method

The gel content (crosslinking) analysis follows in principle the steps recommended in ASTM D2765-90 for crosslinked ethylene plastics. Due to the unique nature of UHMWPE, the following conditions have been modified or added:

(1) The extraction solvent is xylene. But the extraction temperature is at the xylene's boiling temperature (138 to 141°C), rather than at the controlled 110°C as used in ASTM. The higher temperature helps to dissolve UHMWPE.

(2) A 400-mesh stainless steel cloth is used to wrap the UHMWPE sample. A 120-mesh stainless steel cloth (more opened) is recommended in ASTM. Samples with a low gel content may leak out of the cage at the later stage of extraction.

(3) The moisture content of the sample is controlled to be "below 10 %" before and after extraction for sample weighing steps.

(4) An IR moisture analyzer (dryer) at 80°C is used to remove xylene after extraction. A vacuum oven at 150°C is recommended in ASTM. The IR moisture analyzer monitors the drying and stops when a constant weight is detected. (During the test, the weight loss of the sample is continuously monitored within a moving window of time. When the loss of weight within the window is less than the set % of initial weight, an integrated slope function provides an automatic endpoint to the test).

Modified procedure for gel content determination.

1. Each UHMWPE sample for gel content determination consists of well-cut slices (8-16 slices for round rod and 2-4 for rectangular rod) **5 microns** thick and weighs between **450 milligrams** as a whole. Up to **9 samples** can be extracted at one time. The samples should be placed in a desiccating chamber if they cannot be weighed immediately.

2. To cut the slices, use a razor blade to remove the edge or surface not to be included in the analysis.

3. Cut about **88.90 by 139.70 mm** of stainless steel wire mesh, about 400 US gage. The weight of the mesh should be between **1515 mg and 1530 mg**. Fold the length in half, then the width as many times allowed by its length to make a cage to enclose the PE samples. Turn one end twice, then the other. Then use a thread of wire to secure tightly and to hold the sample in the flask.

4. Weigh the clean, dry sample **(M1 = 50 mg).** Count the number of slices while loosely packing them into the opened cages. Weigh the sample and the cage **(M2 = 1560-1580 mg).**

5. Pass a length of stainless steel wire through the condenser column attaching an identifier tag at the top end and the caged sample at the bottom end.

6. Weigh and place **10 grams** of antioxidant into a flask and a few boiling chips to create agitation for even boiling.

7. Slide caged samples into flask one by one.

8. Add about **1.8 liter of xylene** into the flask.

9. Insert condenser column into flask neck. Make sure that all connections (joints and rubber hosing) are tight and that cooling water is circulating through column. Make sure that sample cage is completely submerged in solvent and not touching any part of the flask.

10. **Note the time and the date (t_0).**

11. Turn on heating mantle (set to 9). After about 20 minutes, the solvent should be at a vigorous boil. When this occurs, **note the time and the date (t_1).**

12. Allow extraction to proceed for 20 hours. If needed, prepare extra identifier tags for the removed samples.

13. After 20 hour extraction, stop the heating mantle at the initial time noted (t_0). After 5-10 minutes, proceed to #14 .

14. Separate flask and column. Remove the cages, cut them one by one from flask, and attach them to their respective identifier tags.

15. Place the caged samples to be dried in the moisture analyzer IR-200 (Denver Instrument Company). Set the temperature at 80 degrees. The drying time varies between 15 minutes and 1 hour.

16. Remove the samples and put them in the desiccating chamber to be weighted.

17. Weigh cool dry caged samples **(M3).**

The percent extract is given by

$$\%E = \frac{M2 - M3}{M1} \times 100$$

The percent gel content is 100 - %E

2.6 Formulae

For both methods, we used the formula presented in the ASTM standard.

Percent extract (% E) = [(w2 - w3) / w1] x 100

Percent gel content = 100 - % extract

W1= weight of the pouch (original specimen)

W2= weight of the specimen and the pouch

W3= weight of the specimen and the pouch after extraction and drying

2.7 Rods Dimensions

Figures [1,2, & 3, in the next pages] show the two types of rods we have used during the study. Figure[1] shows the profile used for the round rod. The whole round rod measures approximately 67.75 millimeters in diameter. The skin or outer region is the area between 67.75 millimeters and 59.46 millimeters, the middle region is between 59.46 millimeters and 47.52 millimeters. The inner region represents the area on the rod which has a maximum diameter of 47.52 millimeters. When not specified as profiles, the samples consist of microtomed slices taken right from the surface.

Figure [2] shows the dimension of the typical rectangular rod used. It measures 88.90 millimeters in length, 63.50 mmillimeters in height, and 63.50 millimeters in width.

In general our samples are taken in the region referred to as inner which is the one 3 millimeters off all 4 sides of the block.

Figure[3] shows a schematic of how the rectangular rod profiles was done using the average depth for each five slices up to about 600 slices. Then the cuts were skipped to 1, 3, 5, 10, and 15 millimeters into the height of the rod.

Round Rod Dimensions for Profiles

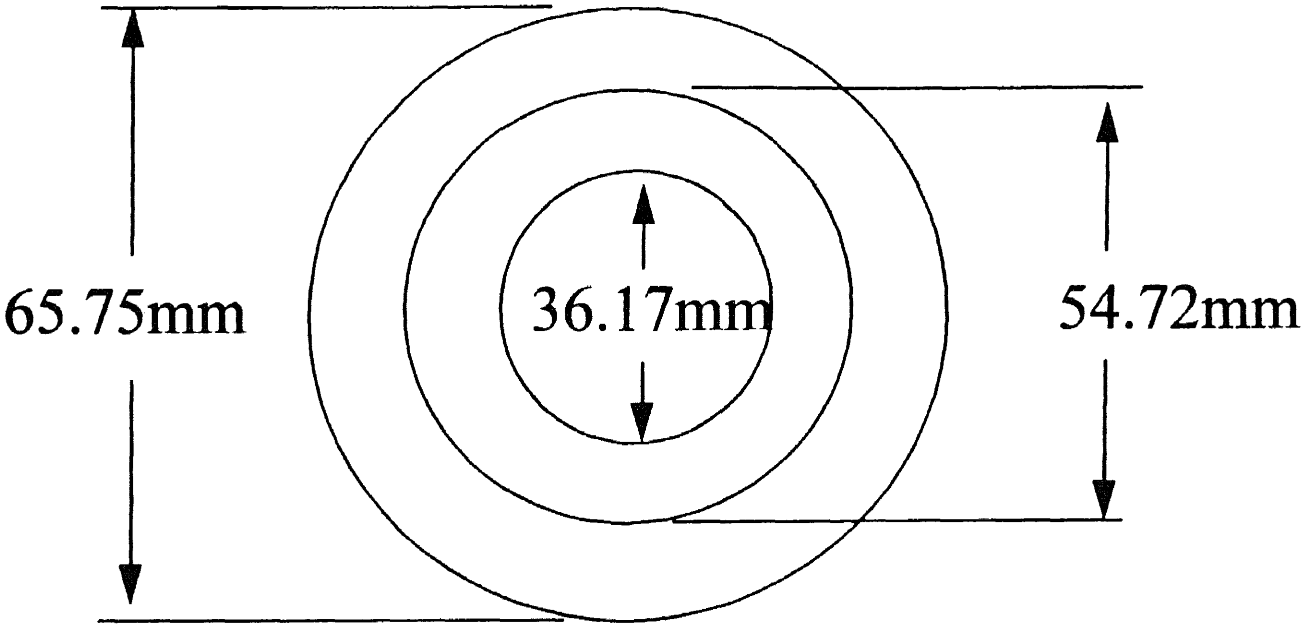


FIGURE 1.DIM & PROFILE of ROUND ROD

Rectangular Rod Dimension and Samples

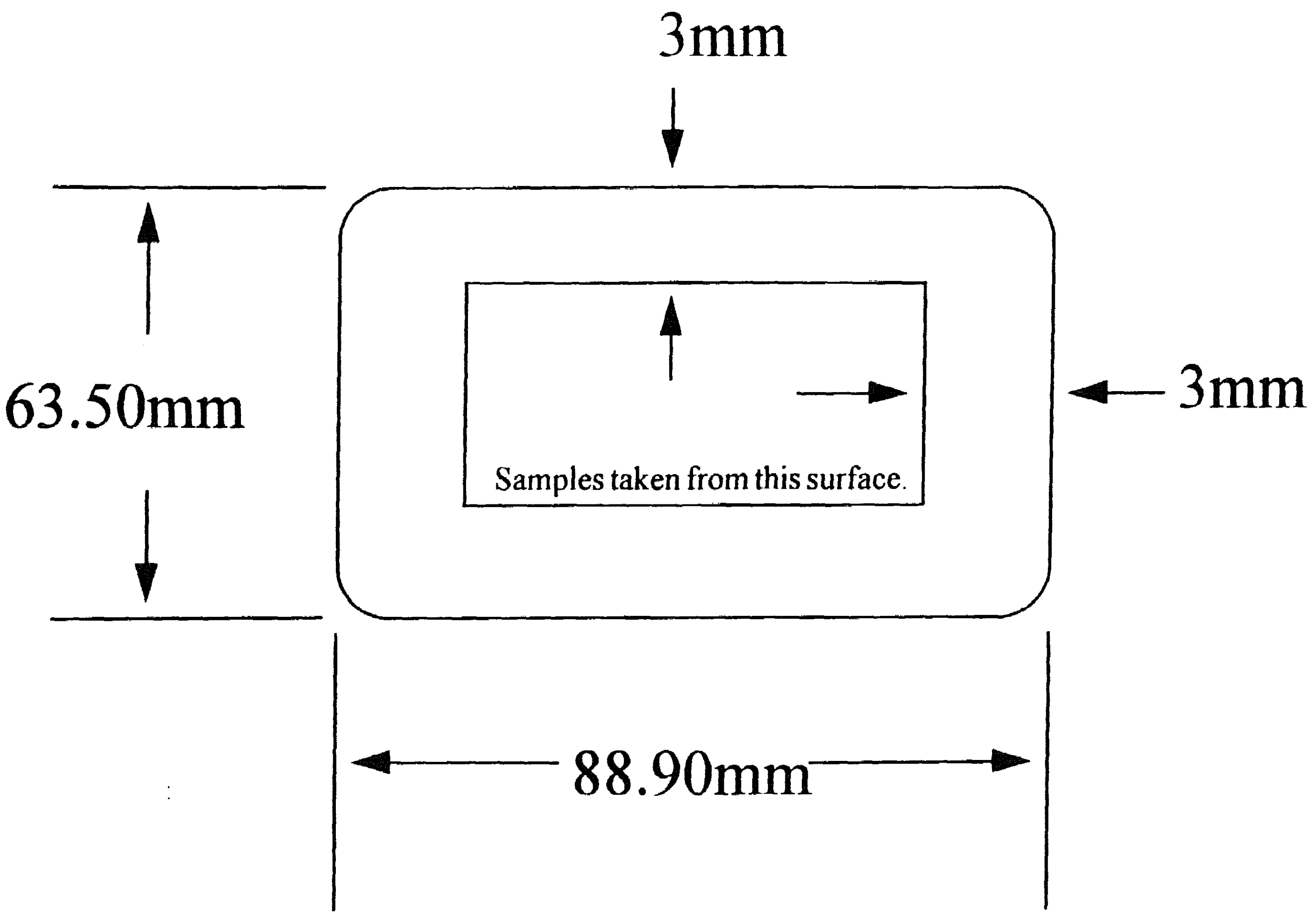
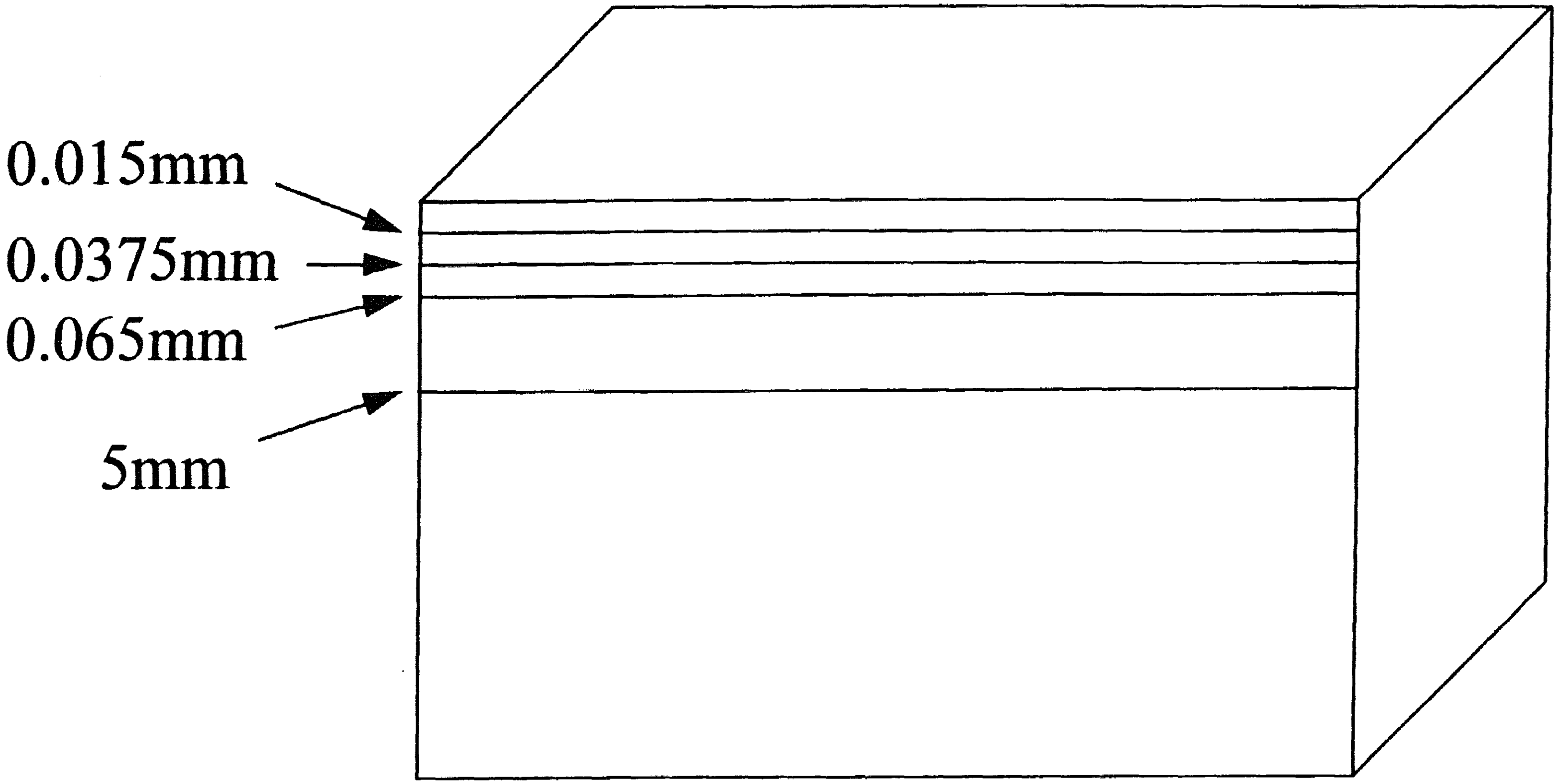


FIGURE 2. PROFILE of RECT ROD

Rectangular Rod Dimension for Profiles



All slices are 0.005mm thick.

FIGURE 3.DIM for PROFILE of RECT ROD

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Protocol Development

Table 1 on page 30 lists all the most important experiments with the conditions and varying elements in our progress toward a procedure that satisfies our gel content determination methods of differently processed UHMWPE. Many of the earlier experiments and some newer ones were used as part of the modified protocol development and also as the main ingredients to determine the relationship between gel content and the manufacturing process of the different UHMWPE samples.

3.1.1 Weight Control in Samples and Cages

In work done by other investigators on UHMWPE extraction procedure, elements such as the weight of the cages and samples were not very well controlled. This created problems in the accuracy of the numbers generated as the percent gel content. One same experiment repeated 2 or 3 times yielded different results every time. Therefore, the first parameters we tried to control were the weights of the elements. Our tolerance for the wight was plus or minus 1 mg. An example of three good samples weight in milligrams is: 299.98, 300.01, 299.01 Previously, an acceptable set was: 279.82, 285.67, and 300 although the difference in weight of the sample is as much as 20 mg. We did the same for the cages.

TABLE 1.EXPERIMENTS AND CONDITIONS

expt #	Date	Book page #	Polyethylene Condition					Extraction Condition							
			Batch#	Lot #	Material	Process condition	Rod shape	sample weight	solvent volume(L)	PE concent. (mg/l)	mesh size	folding method	Humidity control	extraction time	drying method
1	2/5/96	11	853803	yp006	PolyHi	525 degrees	round	300	1.2L	1000	120US gage	staple / 3 folds	no	24hours	oven overnite
2	2/12/96	16	853803	yp006	PolyHi	525 degrees	round	300	1.2	1000	120US gage	staple / 3 folds	no	24 hours	oven overnite
3	2/20/96	18	852713	wp-058	PolyHi	standard	round	300	1.4	1071	120US gage	staple / 3 folds	no	24 hours	oven overnite
4	2/28/96	24	853803	yp006	PolyHi	525 degrees	round	300	1.4	1071	120 US gage	staple / 3 folds	yes	24 hours	oven overnite
5	2/28/96	25	853803	xp050	PolyHi	standard	rect	300	1.9	1071	120 US gage	staple / 3 folds	yes	24 hours	oven overnite
6	6-Mar	28	853803	yp006	PolyHi	525 degrees	round	300	3.6	333	400 US gage	staple / 4 layers	yes	24 hours	oven overnite
7	3/19/96	32 &34	853803	xp050	PolyHi	air irradiated	rect	150	1.8	250	400 US gage	staple / 4 layers	yes	10 hours	oven overnite
8	3/20/96	33 & 35	853803	xp050	PolyHi	unirradiated	rect	150	1.8	250	400 US gage	staple / 4 layers	yes	10 hours	oven overnite
9	4/2/96	40	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	staple / 4 layers	yes	20 hours	moist analyzer
10	4/8/96	41	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
11	4/9/96	42	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
12	4/10/96	45	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
13	4/11/96	46	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
14	4/17/96	49	853803	xp050	PolyHi	unirr,air irr, & stabilized	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
15	4/24/96	53	853803	xp050	PolyHi	unirradiated	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
					PolyHi	500 & 525 deg	rect	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
16	5/6/96	55	853803	xp050	PolyHi	unir	rect	60	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer
17	5/6/96	56	853803	yp006	PolyHi	unir	round	50	1.8	250	400 US gage	folded/ 10 layers	yes	20 hours	moist analyzer

In the first few experiments attempted[1-5], the No 120 US gage stainless steel wire cloth (corresponding to approximately .09 millimeter) was used as suggested by the ASTM method. In each one, as the samples were cooled down to be dried, traces of non dissolved UHMWPE were observed. This phenomenon was attributed to :

(1) Leakages of the material through the cages

(2) The incapacity for the volume of xylene used to completely dissolve the amount of material in the cages.

This gave rise to small amount of gel content in our samples as shown in Table 2, 3, 4, and 5 .

To diminish the extent of the leakages occurring, we used the No 400 US gage stainless steel wire cloth with finer grain size from experiment 6 to 17 (corresponding to .04 millimeter). As table 2 and 5 shows, there is a big difference for the same sample.

In all the experiments involving the 120 US gage, leakage of the samples occurred constantly. By introducing the much finer 400 US gage, we also increased the number of layers (by folding instead of stapling) that the dissolved UHMWPE needed to go through in order to leave the right amount of gel.

3.1.2 Determination of the Maximum Solubility of Xylene

Since precipitation of the samples was occurring consistently in all the instances where the 120 US gage wire was used, in order to find out the maximum amount of xylene needed to dissolve our caged UHMWPE, an experiment was designed which told us the

Table 2 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD (ROUND-525 DEG-INERT-EXPERIMENT: 1,2, & 4)

SAMPLE ID	GEL CONTENT (%)
SAMP 1	20.34
SAMP 2	19.55
SAMP 3	23.00
SAMP 4	13.40
SAMP 5	16.16
SAMP 6	22.84
SAMP 7	25.58
SAMP 8	26.40
SAMP 9	21.52
SAMP 10	21.39
SAMP 11	21.74
MEAN	**21.08**
STANDARD DEVIATION	**3.77**

NOTE: POLYHI EXTRUDED ROUND ROD (2.5 INCH DIAMETER-EXTRUSION TEMPERATURE 525 DEGREES F IN INERT ENVIRONMENT-120 US GAGE MESH)

TABLE 3 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD(ROUND-460 DEG-AIR IRRADIATED-EXPERIMENT 3)

SAMPLE ID	GEL CONTENT (%)
SAMP 1	9.65
SAMP 2	9.49
SAMP 3	7.47
MEAN	**8.87**
STANDARD DEVIATION	**1.22**

NOTE: POLYHI EXTRUDED ROUND ROD (2.5 INCH DIAMETER-EXTRUSION TEMPERATURE 460 DEGREES F IN AIR-120 US GAGE MESH)

TABLE 4 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD (RECTANGULAR-STANDARD-460 DEG-AIR IRRRADIATED-EXPERIMENT 5)

SAMPLE ID	GEL CONTENT (%)
SAMP 1	37.84
SAMP 2	43.35
SAMP 3	40.67
SAMP 4	45.62
SAMP 5	50.46
MEAN	**43.59**
STANDARD DEVIATION	**4.82**

TABLE 5 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD (ROUND-525 DEG-INERT-EXPERIMENT 6)

SAMPLE ID	GEL CONTENT (%)
SAMP 1	10.88
SAMP 2	2.21
SAMP 3	2.39
SAMP 4	3.92
MEAN	**4.85**
STANDARD DEVIATION	**4.09**

NOTE: (1) XYLENE WAS REPLACED AFTER THE FIRST 6 HOURS OF EXTRACTION
(2) A FINER MESH (400 US GAGE STAINLESS STEEL WIRE) WAS USED

TABLE 6 : GEL CONTENT PROFILES OF EXTRUDED UHMWPE ROD - EFFECT OF GAMMA IRRADIATION(RECTANGULAR-EXPERIMENT 7 & 8)

LAYERS	GEL CONTENT (%) UNIRRADIATED	GEL CONTENT (%) AIR IRRADIATED
OUTER	18.2	75.41
MIDDLE	79.33	76.29
INNER	75.42	76.65

NOTE: AIR IRRADIATION IS DONE BY GAMMA RAYS AT 2.5 MRADS(400 US GAGE MESH) right amount needed for both elements (cages and samples) while also allowing us to know the time needed for the extraction.

In the experiments,1.8 liter of xylene was normally used to extract 1200 mg of PE. Trying to remedy to the precipitation problem of the samples upon cooling, the amount of xylene was doubled. This allowed to write by ratio that 33 mg of materials should dissolve in 100 cc of xylene or that 333 mg would dissolve in 1 liter (1000 cc). It was already observed that the maximum weight of PE to dissolve in 1 liter of xylene should be between 200 mg and 350 mg. Based on the amount of precipitation in the xylene (clear = no precipitate; cloudy = precipitate) when the liquid was cooled, we were able to elaborate on the status of the extraction (complete or incomplete).

The weight normally used in the procedure was 300 mg. The weights used for the solubility experiments were 200 mg, 250 mg, 300 mg, and 350 mg. Using the Poly Hi standard (unirradiated) samples, it was observed that for the 200 mg and the 250 mg samples, boiling followed by immediate cooling of the solution produced no precipitation[figure 4]. But when the weight increased to 300 mg and 350 mg, although the precipitation was at different levels, it was observed in both flasks. This observation led to conclude that the maximum weight to use was between 250 mg and 300 mg. By monitoring the time, it was determined that for an unprocessed UHMWPE, it took between 2 to 4 hours for the extraction to be complete.

Following that experiment, the weight of the samples and the amount of xylene was successfully increased from 1200 mg (4 samples x 300 mg) in 1.2 liter to 450 mg (9

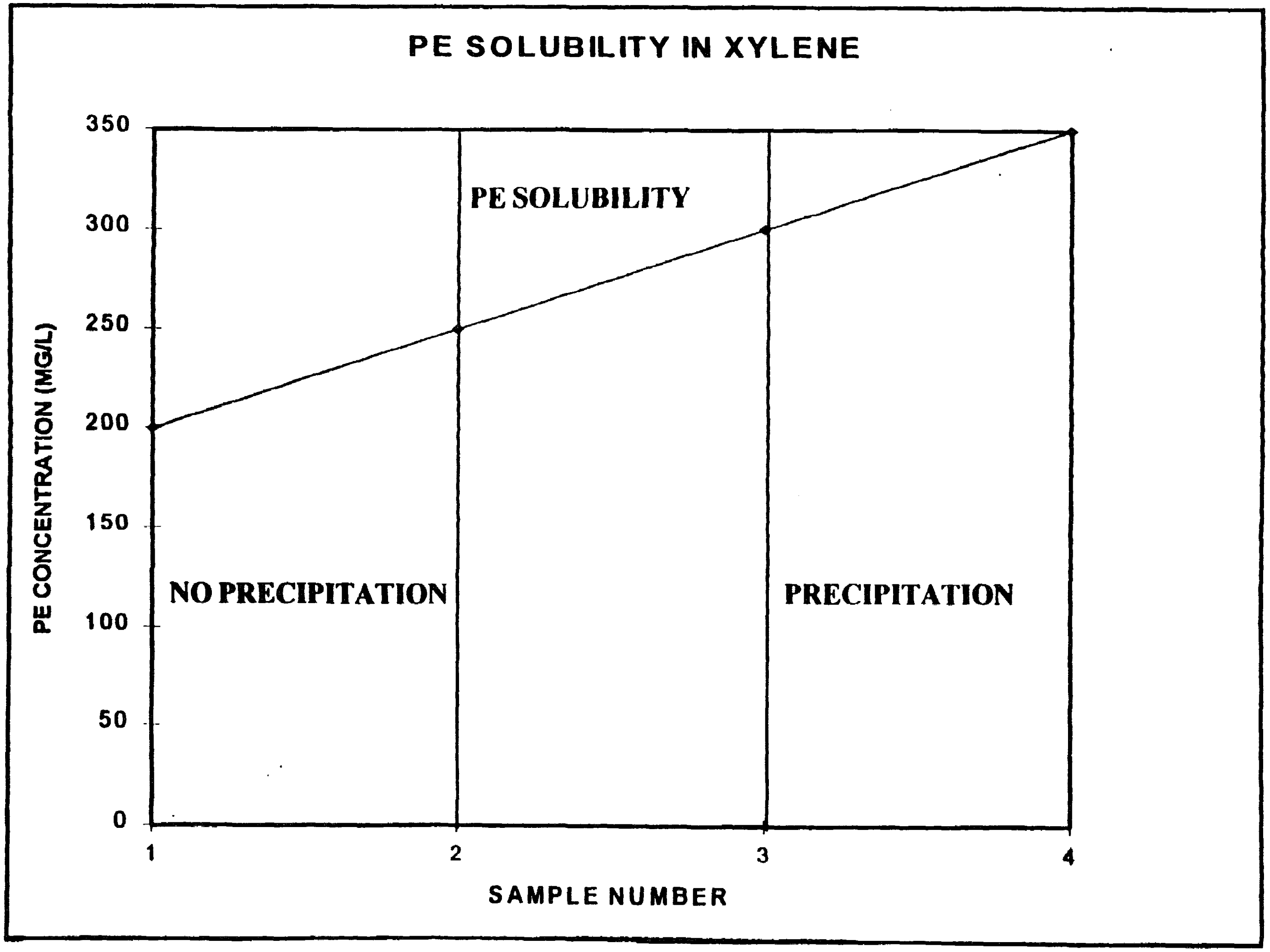


FIGURE 4.UHMWPE SOLUBIITY In XYLENE

samples x 50 mg) in 1.8 liter. Doing so allowed complete dissolution of the UHMWPE samples while leaving the right amount of gel content (Table 7-10 show these results).

The main consequence of this experiment was that it allowed to reduce the weight of material used for the volume of solvent (1.8 liter) in our extraction and therefore maximized the extraction capacity. It also allowed to reduce the time needed for the extraction for the other processed UHMWPE.

3.1.3 Drying and Moisture Absorption Conditions

The drying method suggested by the ASTM procedure was long. It was not necessary to use overnight drying under vacuum. We purchased the moisture analyzer (IR 200 by Denver Instrument). It reduced the drying time by a full day since it only needed a maximum of one hour to dry the samples.

All these major changes (the weight control system, the new folding method, determination of the maximum concentration of PE in xylene, the wire mesh size change) contributed to having an extraction method rivaled by no others available at this time on the market. This final modified version presented in the materials and methods section 2.5 have allowed to investigate the crosslinking capacity of some known materials as well as some new enhanced types under study at this moment in the research and development laboratories of Howmedica.

The following table summarizes the major problems encountered with the procedure and the modifications brought:

Modifications to the ASTM Procedure

PROBLEM	MODIFICATIONS
WEIGHT	More control upon preparation
UHMWPE LEAKAGE	use of finer mesh and folding mechanisms involving more layers and no stapling
UHMWPE PRECIPITATION	Determination of the maximum UHMWPE solubility in xylene
DURATION OF EXTRACTION	-Better sample preparation (folding) -Solubility of PE in xylene
MOISTURE ABSORPTION	Below 10% humidity approach during preparation
DRYING	Use of moisture analyzer (IR 200)

3.2 Correlation Between Processing Conditions and Gel Content

As mentioned earlier, a working tool was needed to measure the right amount of gel content in differently processed UHMWPE. As a result of the innovations, it was possible to determine accurately the gel content of many treated samples.

3.2.1 Effect of Mesh Size

This was a major breakthrough in the efforts toward a new procedure. It had the biggest impact in the results. Experiments 1,2, and 4 were done using the 120 US gage wire while experiment 6 and 17 were done with the 400 US gage. The results are strikingly different. It was thought that the percent gel content for the first experiments (Table 1, page 30) could not have been that high due to the treatment the rods had received. The standard is unirradiated and could not have promoted crosslinking and the 525 although extruded in an inert atmosphere was not stored in one and therefore could not have contained too much gel. So, experiments 3 and 17 using the same material confirmed the inaccuracy of the percent gel content using the No 120 US gage mesh as opposed to the No 400 and the results obtained represent the right percentage of gel content.

3.2.2 Effects of Extruded Rod Shape

The two types of extruded rod shapes (by the ram extrusion machine) in this study are: round and rectangular. Rectangular rods contained more gel than round as is shown in table 2 (average 21.08%) and table 4 (average 43.59%) on pages 32 and 33. It usually involves more power, therefore higher stress and flow rate in order to extrude the rectangular shape rod. Since these elements along with radiation are accountable for possible crosslinking, it is normal that a rectangular rod would yield more gel.

It is to be noted that the samples from the rectangular rod in table 4 were extracted using the coarser 120 US gage wire. That will explain why the gel percent of this unirradiated rod is slightly high.

3.2.3 Effects of Different Extrusion Temperature

- *460 °F*

These are the poly Hi samples. They are unirradiated and are extruded at 460 °F. Since they are not treated in any medium, their gel content is relatively low. (Table 2 and 9)

- *500 °F*

The percent gel content of the 500 °F extruded samples is high (Tab 9 and fig 5). It is so because of the conditions of the rods during the extrusion process. Since no oxygen is present during the irradiation process, free radicals combine with other free ones close by resulting in crosslinking of the material. As the whole process is done in an inert (nitrogen) environment, there are more possibilities for crosslinking to occur.

- *525 °F*

The 525 °F extruded rod should be low in gel content as table 1,2, and 8 show. Here, it is so because contrary to the 500 °F which was stabilized and stored in nitrogen, the 525 °F was exposed directly to air (oxygen) immediately after extrusion. Therefore the oxidation effect is seen in the outer surface of the material which is more inclined to be

TABLE 7 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD-EFFECT OF RADIATION PROCESS(RECTANGULAR-EXPERIMENT 9)

SAMPLES	**GELCON(%)**	**SAMPLES**	**GEL CON (%)**	**SAMPLES**	**GEL CON (%)**
UNIR 1	12.56	AIR IR 1	93.38	STABLE 1	98.58
UNIR 2	5.06	AIR IR 2	89.72	STABLE 2	102.57
UNIR 3	8.17	AIR IR 3	91.72	STABLE 3	98.63
MEAN	**8.60**	**MEAN**	**91.61**	**MEAN**	**99.93**
STD DEV	**3.77**	**STAN DEV**	**1.50**	**STAN DEV**	**1.87**

NOTE: STABILIZATION PROCESS CONSISTS OF IRRADIATION IN AN INERT ENVIRONMENT AND STABILIZATION AFTER IRRADIATION(SAMPLES ARE FROM CENTER-400 US GAGE MESH)

TABLE 8 : GEL CONTENT PROFILE OF EXTRUDED UHMWPE ROD-EFFECT OF RADIATION PROCESS(RECTANGULAR-EXPERIMENT: 10, 11, 12, 13, & 14)

DEPTH(MM)	**GEL CON (%) UNIRRADIATED**	**GEL CON (%) AIR IRRADIATED**	**GEL CON (%) STABILIZED**
.0.015	7.56	16.62	50.64
0.0375	10.64	45.06	79.56
0.065	7.65	89.40	89.54
0.09	7.34	84.64	96.58
0.115	9.17	96.90	98.24
0.14	8.09	90.65	99.71
0.16	7.28	89.86	98.69
0.1775	5.62	96.28	100
0.195	6.71	93.33	93.14
0.21	11.56	88.85	99.8
0.225	7.18	98.45	100
0.24	6.7	97.02	100
1	3.42	97.10	100
3	17.59	100	100
5	61.18	100	100
10	71.83	100	100
15	76.11	100	100
20	74.45	100	100

NOTE: SAMPLES WERE MICROTOMED FOR THE PARTICULAR DEPTH

TABLE 9 : GEL CONTENT PROFILE OF EXTRUDED UHMWPE ROD-EFFECT OF THE EXTRUSION CONDITION(ROUND-EXPERIMENT 15)

DEPTH(MM)	**GEL CON (%) 500 DEG F**	**GEL CON (%) 525 DEG F**
OUTER(60.99)	81.30	30.71
MIDDLE(53.49)	89.12	47.17
INNER(45.74)	85.19	58.80
MEAN	**85.20**	**45.56**
STD DEVIATION	**3.91**	**14.11**

NOTE: 500 DEG- ROD WAS STORED IN NITROGEN AFTER EXTRUSION
525 DEG- ROD WAS STORED IN AIR
400 US GAGE WIRE MESH WAS USED

TABLE 10 : GEL CONTENT ANALYSIS OF EXTRUDED UHMWPE ROD - EFFECT OF MODIFIED PROTOCOL(ROUND-POLYHI STANDARD-EXPERIMENT 3 & 17)

SAMPLE ID	**GEL CON (%)**	**MEAN GEL CON (%)**
ASTM-SAMP 1(SURFACE)	9.65	
ASTM-SAMP 2(SURFACE)	9.49	**8.82 (ASTM)**
ASTM-SAMP 3(SURFACE)	7.47	
MODI-SAMP 1(INNER)	42.27	
MODI-SAMP 2(MIDDLE)	32.30	
MODI-SAMP 3(OUTER)	22.06	

NOTE: MODIFICATION IN VOLUME OF SOLVENT- MESH SIZE-SAMPLE WEIGHT-...
ASTM SAMPLES ARE TAKEN FROM THE SURFACE
OUTER LAYER REPRESENTS THE SURFACE IN THE MODIFIED

TABLE 11 : PE SOLUBILITY DETERMINATION

XYLENE VOLUME (L)	**PE SAMPLE WEIGHT(mg)**	**PE CONCENTRATION (mg/l)**	**OBSERVATION**
1	200	200	NO PRECIPITATION
1	250	250	NO PRECIPITATION
1	300	300	SLIGHT PRECIPITATION
1	350	350	MORE PRECIPITATION

NOTE : (1) EXTRACTION TIME IS 4 HOURS
(2) MATERIAL IS POLYHI ROUND, STANDARD, UNIRRADIATED

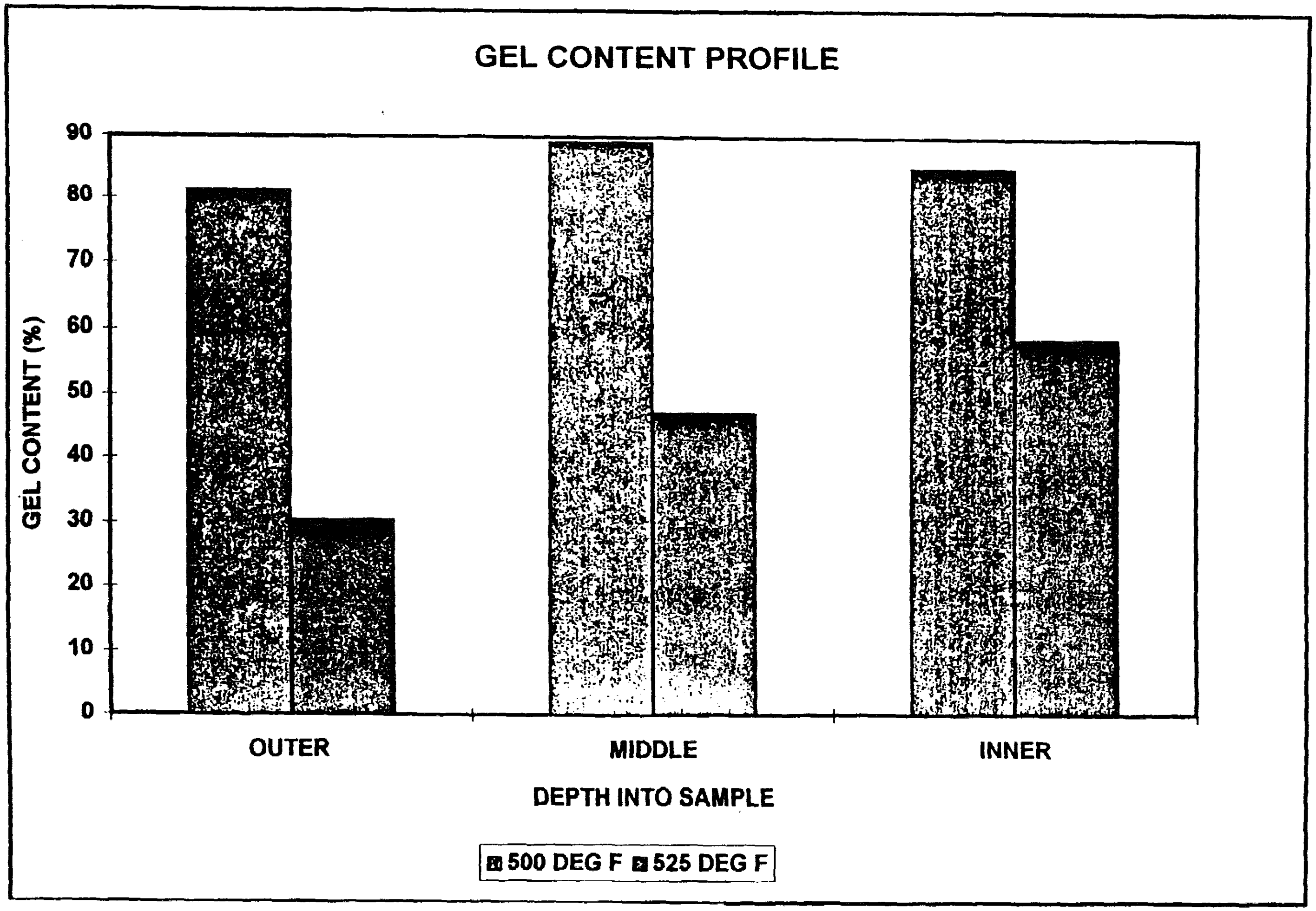


FIGURE 5.PROFILE of 500 & 525 DEG F SAMPLES

affected by its effects. The table shows that in the deeper region, there is little oxidation and that there is a slight increase in the percent gel content (figure 5).

3.2.4 Effects of Different Processing Condition

- *Unirradiated vs Air irradiated vs Stabilized*

Table 6 and figures 6a and 6b show the effect of irradiation with respect to the percent gel content. It is obvious that the treatment in air strongly promotes crosslinking of the material. The gel content on the outer surface of unirradiated samples (18.2 %) and air irradiated samples (75.41%) suggests that the exposure to air alone is not enough for the oxidation process to allow crosslinking. In unirradiated samples, it promotes chain scission while in air irradiated samples, crosslinking is greatly encouraged.

This effect is even stronger when the material is further stabilized as is shown in table 7 and figures 8a, 8b, and 8c). The percent gel content is on an average of 99.3%. This is so because the rod is stored right after irradiation in a mildly elevated chamber that has for effect to eliminate the reactive free radicals (that could have accounted for more chain scission in the material) and promote more crosslinking of the material.

3.2.5 Profiles in Differently Processed Samples

Profiles of samples are the best way to find out where the concentration of the percent gel content is the strongest. The one obtained from table 6 (fig 7) show that the percent gel

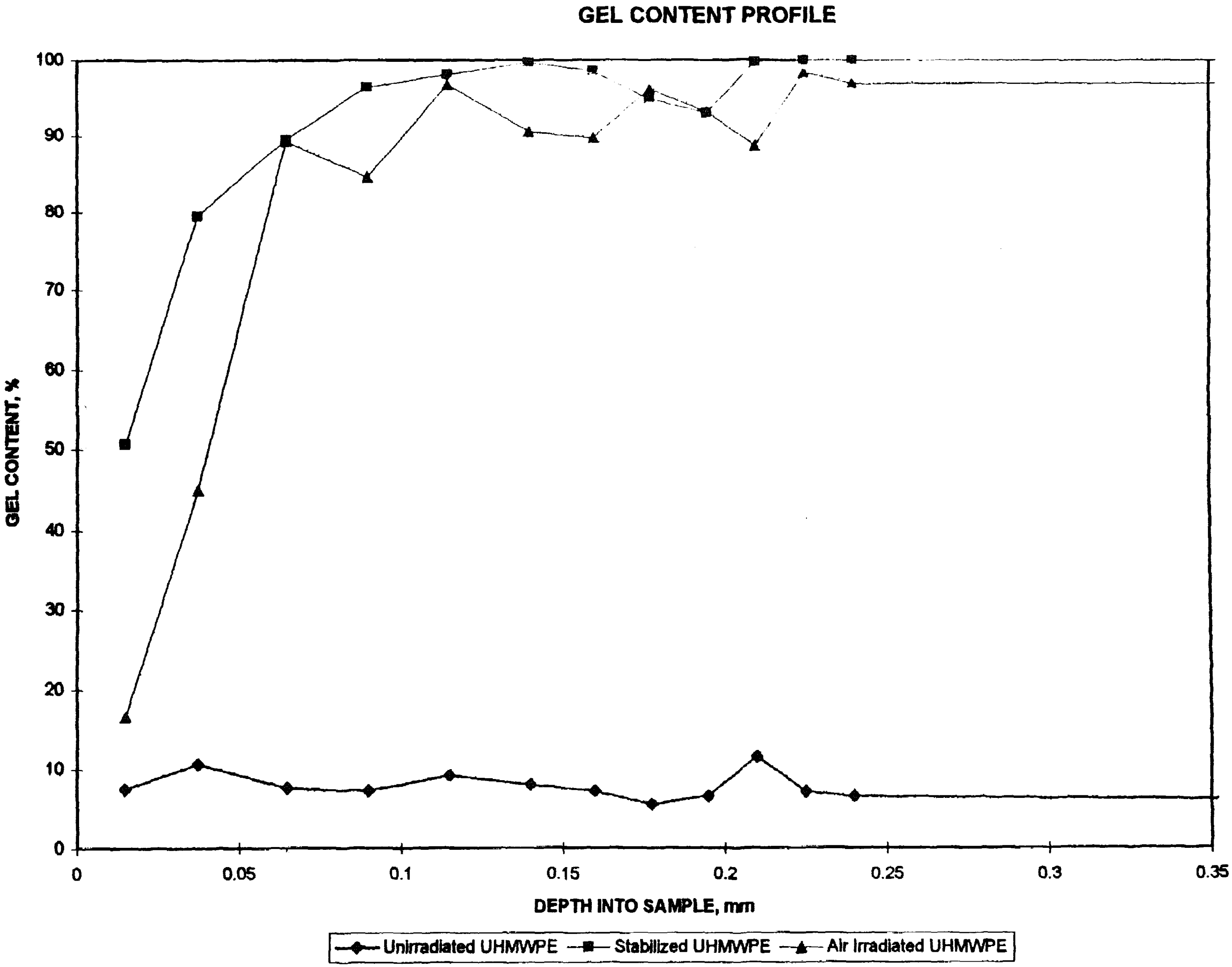


FIGURE 6a.PROFILE 0-.35mm of RECT ROD

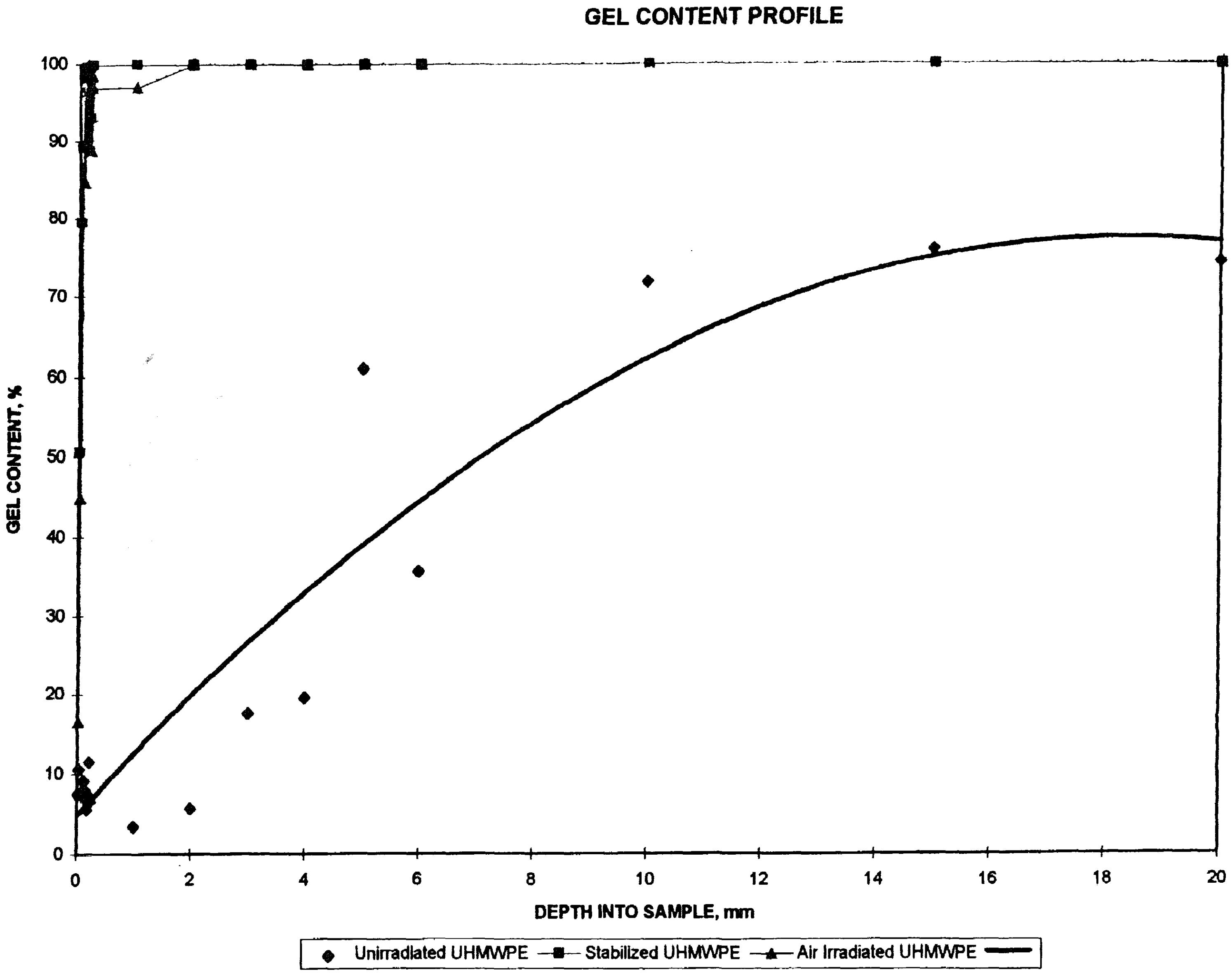


FIGURE 6b.PROFILE 1-20mm of RECT ROD

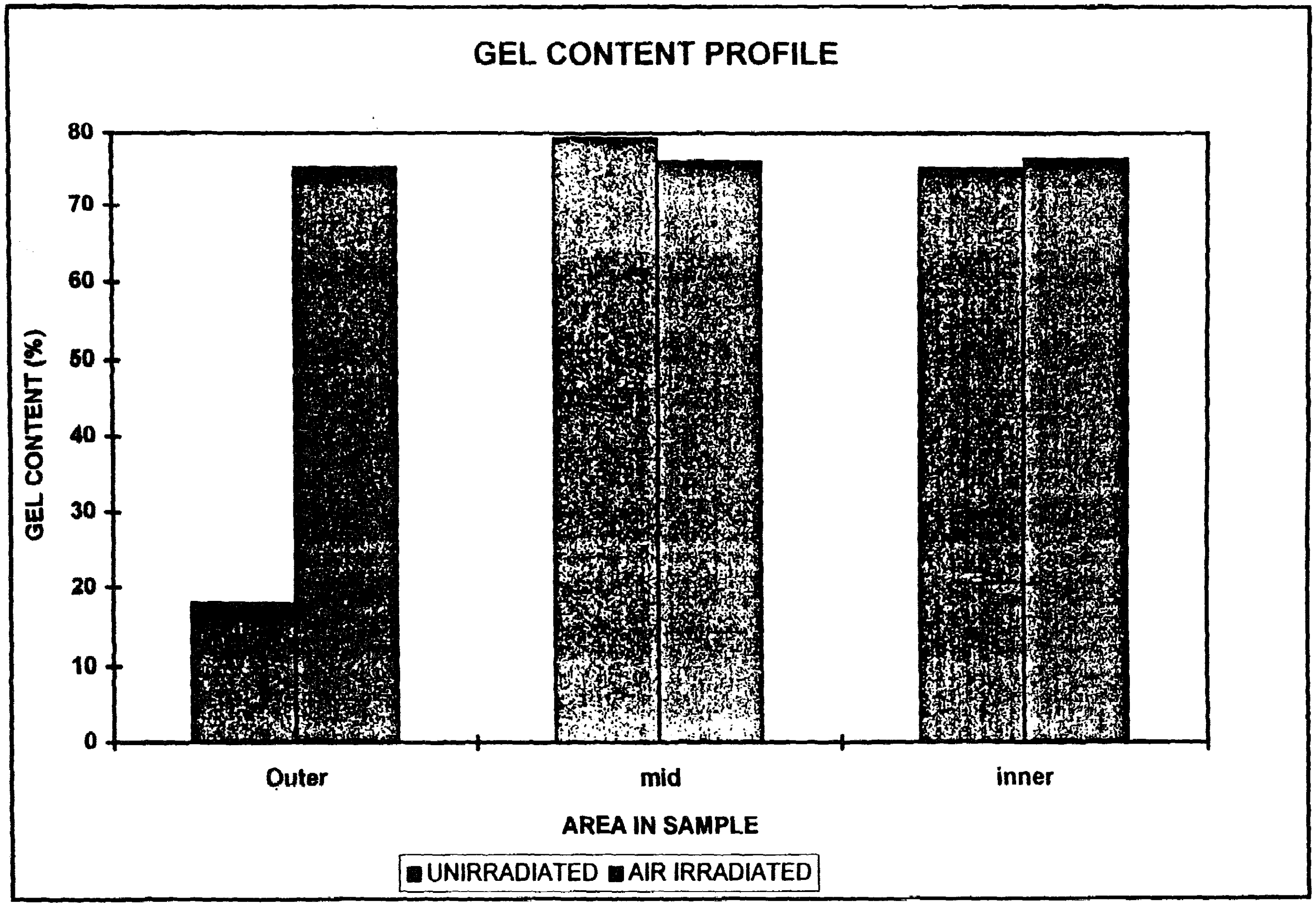


FIGURE 7.PROFILE of UNIR & AIR IR SAMPLES

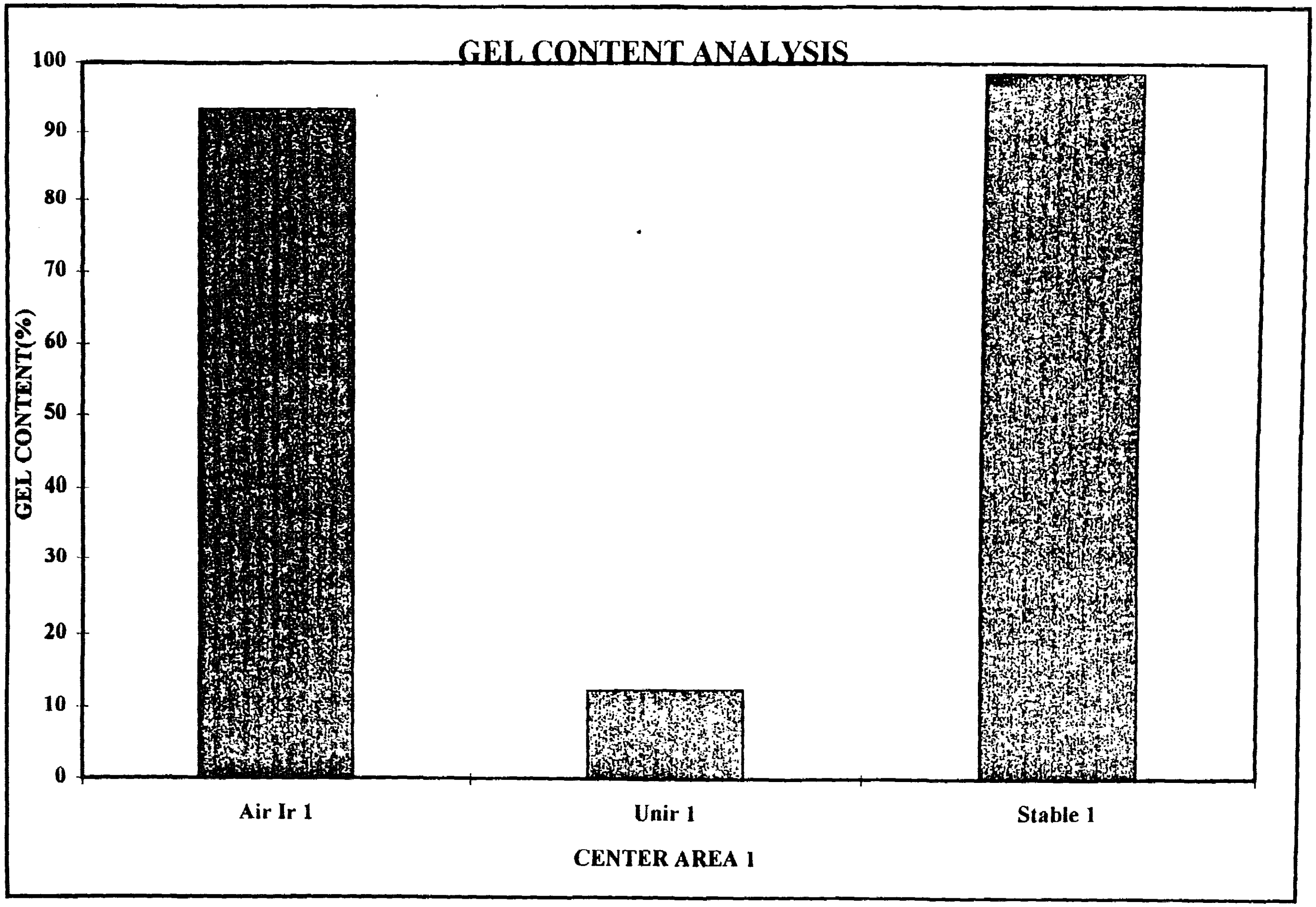


FIGURE 8a.GEL CONT ANALYSIS of CENTER AREA 1

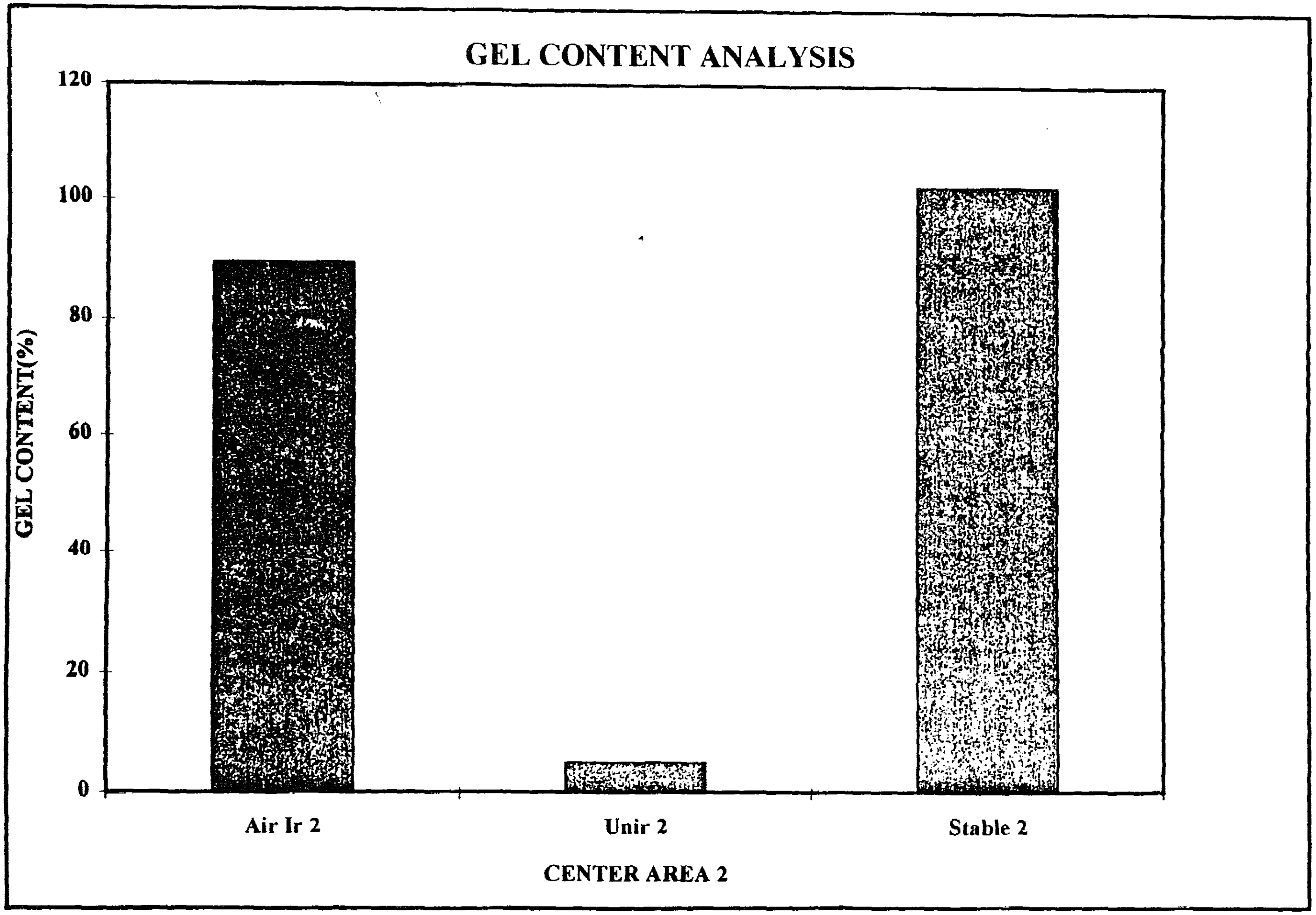


FIGURE 8b.GEL CONT ANALYSIS of CENTER AREA 2

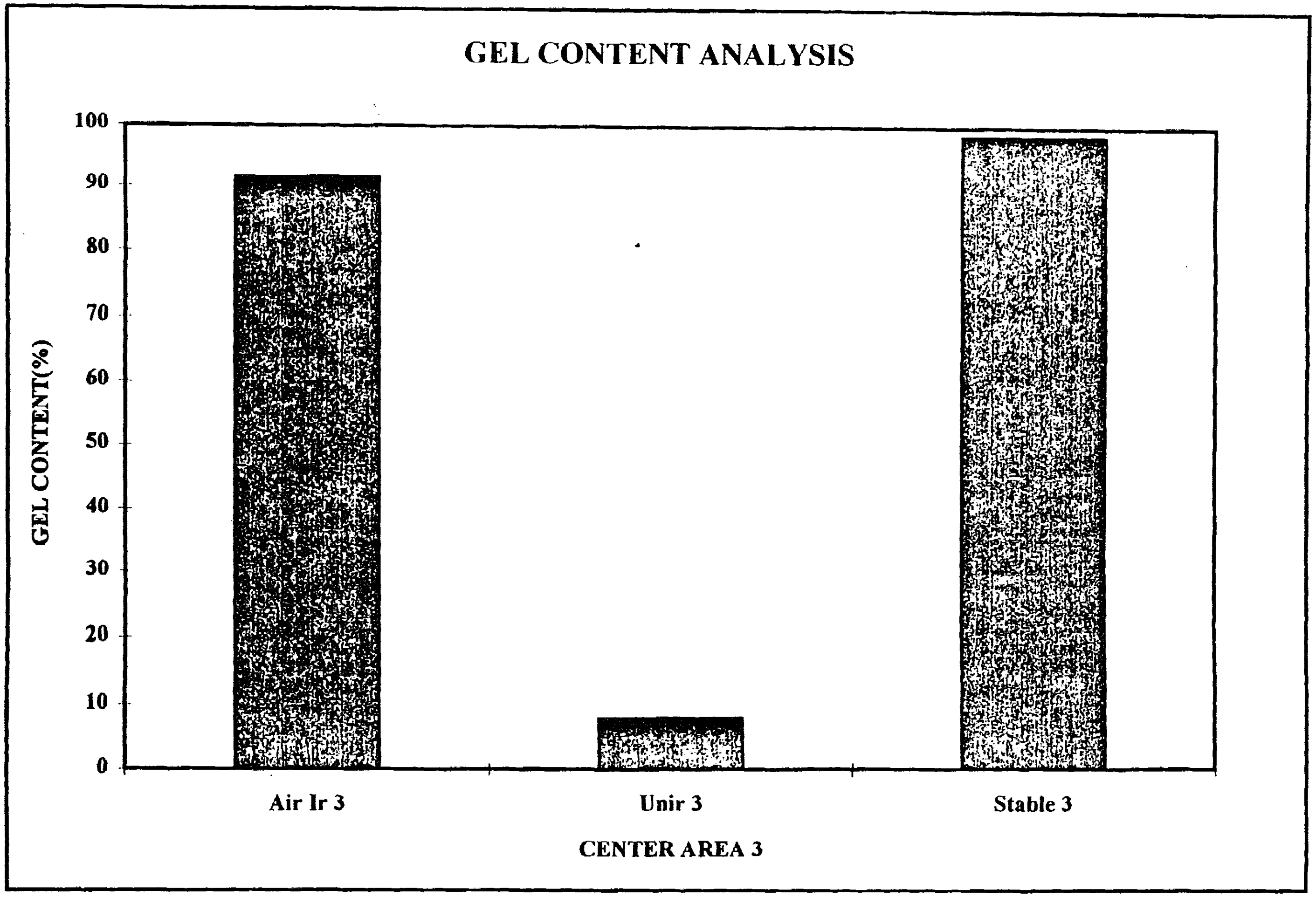


FIGURE 8c.GEL CONT ANALYSIS of CENTER AREA 3

content is lowest on the outer surface of a sample while being highest in the inner surface. This is in coordination with the extent of possible crosslinking occurring not on the outer surface (easier to be oxidized) but in the deeper region more difficult to sustain any oxidation effect.

The profile from table 8 (figure 6a & 6b) confirms this fact and allows to understand the extent of the crosslinking on the microscopic level. As previous tables and graphs have shown, the unirradiated samples are the lowest in gel content followed by the air irradiated samples. The stabilized contain the highest percent of gel.

3.2.6 Comparison

Any of the first 6 experiments can be compared to the last 11 performed to see the effects of the modified procedure. Two that were done at different times using the same type of rods were picked to appreciate the differences between the procedures. The results of experiment 3 and 17 are summarized in table 10. It can be seen that the average percent gel content from the surface is much lower than the outer layer of this same sample. Other results have already supported the fact that 8.82% represents the expected percent gel content for an unirradiated sample because it has not been subjected to any treatment.

The same observation can be made for experiment 1 and 2, and 15 where the gel content using the ASTM specifications is lower than when the modified procedure is used. For the 525 °F rod, it is more likely that the gel content will be high (due to the fact that it was treated in nitrogen) as experiment 15 shows. Since experiments 1 and two were done using the US 120 gage wire, the gel content obtained was not accurate.

CHAPTER 4

CONCLUSIONS

(A) An improved procedure for the determination of gel content of crosslinked UHMWPE has been developed. The improvements make the procedure:

1. More applicable to UHMWPE and can be used for all type of processing conditions.
2. More consistent than any available
3. Easier to follow
4. Quicker (it only takes a maximum of 36 hours as opposed to 72 for the ASTM)

(B) The solubility of UHMWPE has been determined.

(C) The relationship between UHMWPE processing and the percent gel content has been established for the following:

- Rectangular rods contain more gel than round rods
- The gel content is the highest for a stabilized rod and lowest for an unirradiated one.
- The innermost area in the rods contain more gel than the middle and outer area which contains less respectively.

The two main objectives in this study were accomplished.

(1) A modified procedure that works for all types of UHMWPE was developed, and

(2) The relationship between some known UHMWPE samples in relation to their exact amount of percent gel content was finalized.

4.1 Future Work

Meeting these two objectives allow to open up the door for new UHMWPE based material to be developed and tested. Our procedure will help in assessing their ability to crosslink offering better resistance to wear, increased yield and impact strength, and other mechanical properties necessary in implant materials. The next step as a result of this study is to evaporate the solvent obtained from the extraction in order to analyze the dried component. Its structure, composition, and extent of crosslinking will be known through the usage of instruments such as FTIR (Fourier Transform Infrared Spectroscopy) and DSC (Differential Scanning Calorimetry) which will help to better understand the different properties of UHMWPE.

APPENDIX A

SYNTHESIS OF UHMWPE RESIN

Figure 9 presents a flow chart of the manufacturing process for UHMWPE surgical implants. As noted, the synthesis of UHMWPE resin is the first step.

The synthesis method of UHMWPE used today is a low-pressure process initially developed by K. Ziegler of the Max Planck Institute in Muhleim- Ruhr in the early 1950's. Highly pure ethylene as the raw feed is suspended in a hydrocarbon solvent (such as hexane), along with catalysts made from titanium tetrachloride and organo-aluminum compounds. Polymerization of ethylene takes place on the catalyst surface at a temperature below 100 degree C in the absence of air and moisture. The control of molecular weight is achieved by addition of a small amount of hydrogen, or by the adjustment of temperature. On average, about 100,000 ethylene molecules are added onto an active catalyst center to form a molecule of 3 million molecular weight. However, since not every active catalyst site is equally accessible to ethylene molecules, a distribution of molecular weight is present in the finished product. The average molecular weight is around two to six million.

When the polymerization reaction is complete, the solvent suspension medium containing UHMWPE polymer and catalysts goes through a series of centrifuging, stripping, and drying steps, during which the UHMWPE polymer is separated from the suspending agent and other residues. The dry resin powder is then fed into a silo for homogenization and bagging, during which time a small amount of corrosion inhibitor, such as calcium stearate, is added.

There are two companies in the United States producing UHMWPE resin for medical applications: Hoeschst Celanese, supplying hostalen GUR 412 and GUR 415; and Himont, which makes Hifax 1900 and Hifax 1900CM. Hostalen GUR resins are also produced by Hoeschst AG in Germany. Recently, a Japanese company, Mitsui, has also begun to supply UHMWPE.

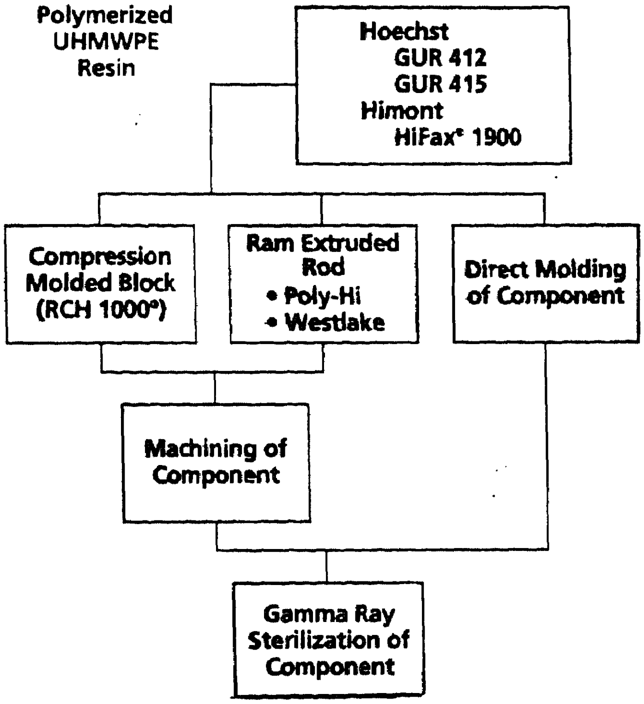


FIGURE 9.FLOW CHART OF UHMWPE PROCESS

APPENDIX B

TYPES OF IRRADIATION PROCESSES

This appendix shows the three types of irradiation processes and the reactions occurring during irradiation, oxidation, chain scission, and crosslinking.

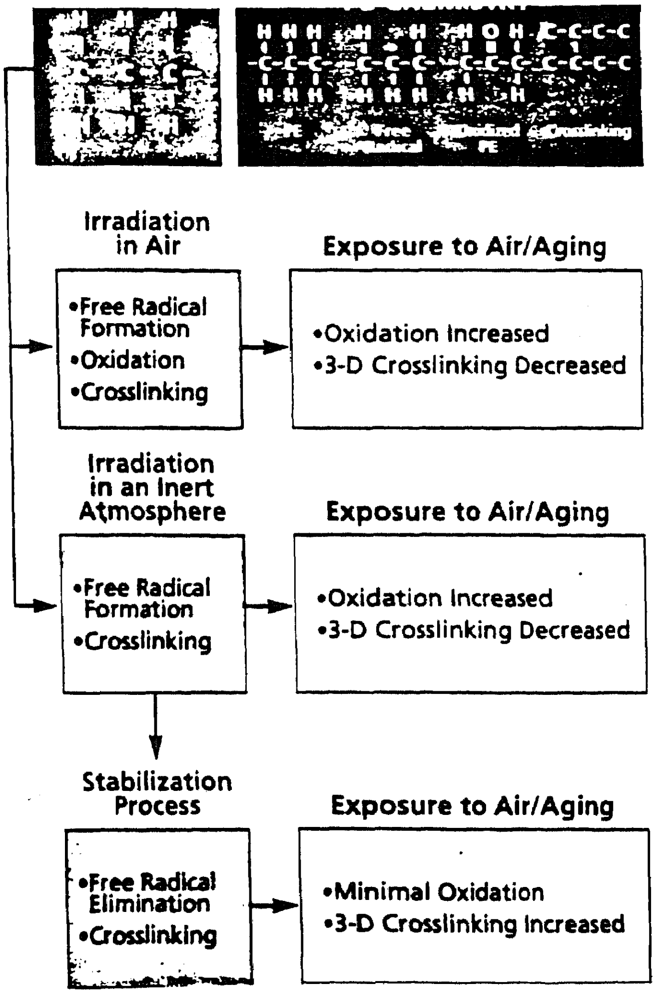
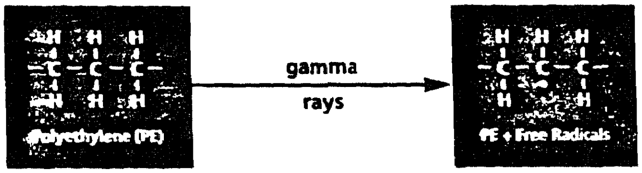


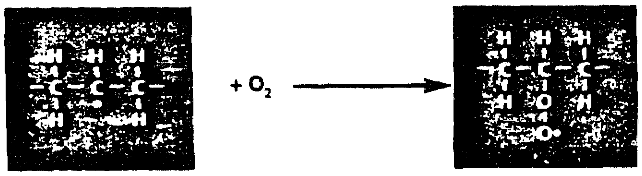
FIGURE 10.DURATION STABILIZATION PROCESS

Gamma Ray Sterilization

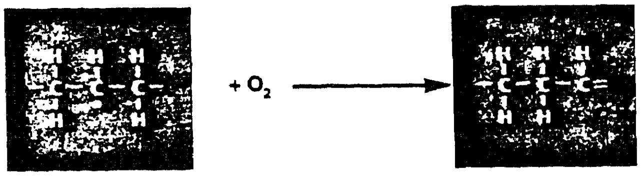
(1a) Irradiation



(1b) Oxidation



(1c) Chain Scission



(1d) Crosslinking

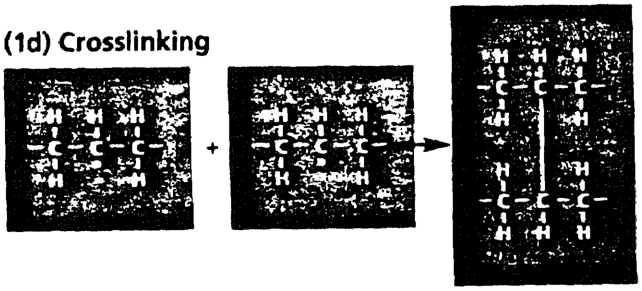


FIGURE 10.(CONTINUED)

REFERENCES

1. R.L. Clough and S.W. Shalaby, "Radiation Effects on Polymers," ACS Symposium Series 475, p55, 1991.

2. D. W. Clegg and A.A. Collyer, *Irradiation Effects on Polymers,* Elsevier Applied Science, London, Chapters 1 and 2, 1991.

3. D. K. Collis, "Long-Term (Twelve to Eighteen-Year) Follow up of Cemented Total Hip Replacements in Patients Who Were Less Than Fifty Years Old," The Journal of Bone and Joint Surgery, Vol 73A pp593-597, 1991.

4. D. A.Miller, "A Technical Report on Ultra High Molecular Weight Polyethylene," Development Department Zimmer Pty. Ltd., USA, pp1-9, 1983.

5. P. Eyerer, D. Rodlauer, and A. Siegmann, *Trends to New Developments in UHMWPE as Biomaterials in Orthopaedic Surgery,* Copyright 1991 by Hogrefe and Huber Publishers, United States, New York, pp236-240, 1986.

6. D. I. R. Kellersonn, *Processing of UHMWPE (Hostalen GUR), UHMWPE as Biomaterials in Orthopaedic Surgery,* Copyright 1991 by Hogrefe and Huber Publishers, United States, New York, pp6-10, 1986.

7. R. D. Ainsworth, "Molded Polyethylene Acetabular Cups," Development Department Zimmer Pty. Ltd., USA, 1983.

8. H. N. Birkraunt, *Synthesis of UHMWPE, UHMWPE as Biomaterials in Orthpaedic Surgery,* Copyright 1991 by Hogrefe and Huber Publishers, United States, New York, pp3-5, 1986.

9. C. de Putter, G. L. de Lange, K. de Groot, and A. J. C. Lee, "Implant Materials in Biofunction," Proceedings of the Seventh European Conference on Biomaterials, Amsterdam, The Netherlands, pp377-380, 1987.

10. E. S. Grood, F. R. Noyes, "Cruciate Ligament Prosthesis Strength, Creep and Fatigue Properties," Journal of Bone Surgery, Vol 58A pp1083-1088, 1976.

11. R. J. Roe, E. S. Grood, R. Shastri, C. A. Gosselin, and F. R. Noyes, "Effect of Radiation Sterilisation and Aging on UHMWPE," Journal of Biomedical Materials Research, Vol 15 pp209-230, 1981.

12. E. S. Grood, R. Shastri, and C. N. Hopson, "Analysis of Retrieved Implants: Crystallinity Changes in UHMWPE," Journal of Biomedical Materials Research, Vol 16 pp399-405, 1982.

13. D. C. Sun, C. Stark, and J. H. Dumbleton, "20th Annual Meeting," Society for Biomaterials. April 5-9. p121, 1994.

14. L. C. Sutula, D. K. Sperling, J. P. Collier, K. A. Saum, and I. R. Williams, "Impact of Gamma Sterilisation in Air and Material Consolidation," In: Symposium III, Hip Society and the Association for Arthritic Hip and Knee Surgery. Orlando FL, February 19, 1995.

15. M. S. Jahan, C. Wang, G. Schwartz, and J. A. Davidson, Journal of Biomedical Materials Research, Vol 25, pp 1005-1017, 1991.

16. D. C. Sun, C. Stark, J. H. Dumbleton, "Polymer Reprints," Vol 35, No. 2, pp969-970, 1994.

17. "Overview and Fundamentals of UHMWPE, No. 1, Facts on UHPWPE Series," Published by Howmedica Inc, Rutherford, New Jersey, Pfizer Hospital Products Group, 1994.

18. "Material Properties, Product Quality Control, and their Relation to UHMWPE Performance, No. 2, Facts on UHMWPE Series," Published by Howmedica Inc, Rutherford, New Jersey, Pfizer Hospital Products Group, 1994.

19. "A Comparative Analysis of the Properties of the Standard and Enhanced UHMWPE, No. 3, Facts on UHMWPE Series," Published by Howmedica Inc, Rutherford, New Jersey, Pfizer Hospital Products Group, 1994.

20. D. C. Sun, and C. Stark, "Non-Oxidizing Polymeric Medical Implant," U.S. Patent No. 5,414,049.

21. R. M. Streicher, *The Behavior of UHMWPE when Subjected to Sterilisation by Ionizing Radiation. In: UHMWPE as Biomaterial in Orthopaedic Surgery,* Toronto: Hogrefe and Huber Publishers, p66, 1991.

22. D. C. Sun, G. Shmidig, C. Stark, and J. H. Dumbleton, 21st Annual Meeting, Society for Biomaterials. March 18-22, p362, San Francisco CA, 1995.

23. A. Charlesby, "The Effect of Ionising Radiation on Polymers," Chapter 2 in Radiation Effects on Polymers. Edited by R. L. Clough and S. W. Shalaby, ACS Symposium Series 475, pp54-59, 1991.

24. Lancaster: *Friction and Wear.* in Jenkins (ed.): Polymer Science, Pages 959-1045, North Holland Publishing Co., 1972.

25. Mckellop, et al., "Accelerated Aging of Irradiated UHMWPE for Wear Evaluations," Trans. Orthop. Res. Soc., 21, 1996.

26. Blunn, et al., "The Effect of Oxidation on the Wear of Untreated and Stabilized UHMWPE," Trans. Orthop. Res. Soc., 21, 1996.

27. R. E. Kirk, and D. F. Othmer Ziegler *Process Polyethylene, Encyclopedia of Chemical Technology,* 5th ed. Copyright by John Wiley and Sons, Canada, Vol 16 pp433-434.

28. A. Frank, M. Kurth, P. Eyerer, and H. L. Federolf, *Method of Testing UHMWPE as Biomaterials in Orthopaedic Surgery,* Copyright 1991 by Hogrefe and Huber Publishers, United States, New York, pp15-22, 1986.

29. G. Akay, T. Tincer, and H. E. Ergoz, "A Study of Low Density Polyethylene Under Natural Weathering Conditions," European Polymer Journal, Vol 16, pp601-605.

30. R. E. Marchant, "On the Biodegradation of Polymeric Materials Intended for Long Term Biomedical Applications," Advances in Biomedical Polymers Symposium, Wester Australia, Perth,1-12, 1989.

31. A. Wang, D. C. Sun, C. Stark, and J. H. Dumbleton, "Effects of Sterilization Methods on the Wear of UHMWPE Acetabular Cups," Howmedica, Inc., Division of Pfizer Hospital Products Group, Rutherford, New Jersey, USA Paper No. 275 5th World Biomaterials Congress, Toronto, Ontario, Canada, May 28-June 2, 1996.