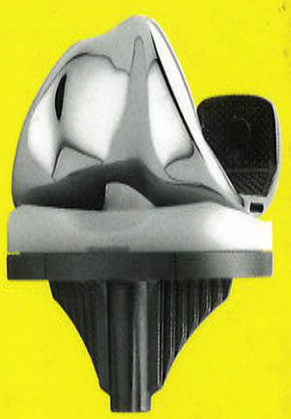
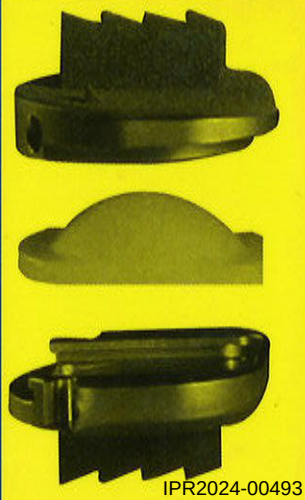
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The UHMWPE Handbook

Ultra-High Molecular Weight Polyethylene in Total Joint Replacement





Steven M. Kurtz, Ph.D.

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Chapter 1

A Primer on UHMWPE

Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a unique polymer with outstanding physical and mechanical properties. Most notable are its chemical inertness, lubricity, impact resistance, and abrasion resistance. These characteristics of UHMWPE have been exploited since the 1950s in a wide range of industrial applications (Figure 1.1), including pickers for textile machinery, lining for coal chutes and dump trucks, runners for bottling production lines, as well as bumpers and siding for ships and harbors. More than 90% of the UHMWPE produced in the world is used by industry.

Since 1962, UHMWPE also has been used in orthopedics as a bearing material in artificial joints. Each year, about 1.4 million joint replacement procedures are performed around the world. Despite the success of these restorative procedures, UHMWPE implants have only a finite lifetime. Wear and damage of the UHMWPE components is one of the factors limiting implant longevity.

UHMWPE comes from a family of polymers with a deceptively simple chemical composition, consisting of only hydrogen and carbon. However, the simplicity inherent in its chemical composition belies a more complex hierarchy of organizational structures at the molecular and supermolecular length scales. At a molecular level, the carbon backbone of polyethylene can twist, rotate, and fold into ordered crystalline regions. At a supermolecular level, the UHMWPE consists of powder (also known as resin or flake) that must be consolidated at elevated temperatures and pressures to form a bulk material. Further layers of complexity are introduced by chemical changes that arise in UHMWPE due to radiation sterilization and processing.

The purpose of this *Handbook* is to explore the complexities inherent in UHMWPE and to provide the reader with a background in the terminology, history, and recent advances related to its use in orthopedics. A monograph such as this is helpful in several respects. First, it is important that members of the surgical community have access to up-to-date knowledge about the properties of UHMWPE so that this information can be more accurately communicated to

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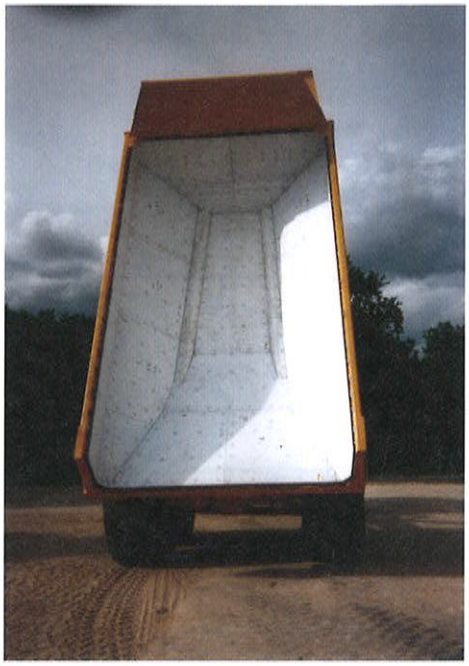


Figure 1.1
Dump truck liner of UHMWPE, an example of an industrial application for the polymer.

their patients. Second, members of the orthopedic research community need access to timely synthesis of the existing literature so that future studies are more effectively planned to fill in existing gaps in our current understanding. Finally, this handbook may also serve as a resource for university students at both the undergraduate and graduate levels.

This introductory chapter starts with the basics, assuming the reader is not familiar with polymers, let alone polyethylene. This chapter provides basic information about polymers in general, describes the structure and composition of polyethylene, and explains how UHMWPE differs from other polymers (including high-density polyethylene [HDPE]) and from other materials (e.g., metals and ceramics). The concepts of crystallinity and thermal transitions are introduced at a basic level. Readers familiar with these basic polymer concepts may want to consider skipping ahead to the next chapter.

What Is a Polymer?

The ultra-high molecular weight polyethylene used in orthopedic applications is a type of polymer generally classified as a linear homopolymer. Our first task is to explain what is meant by all of these terms. Before proceeding to a definition of UHMWPE, one needs to first understand what constitutes a linear homopolymer.

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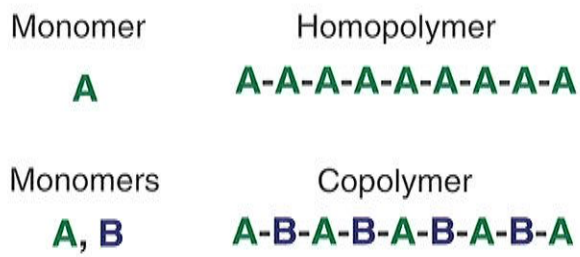


Figure 1.2
Schematics of homopolymer and copolymer structure.

A *polymer* is a molecule consisting of many (*poly-*) parts (*-mer*) linked together by chemical covalent bonds. The individual parts, or monomer segments, of a polymer can all be the same. In such a case, we have a homopolymer as illustrated in Figure 1.2. If the parts of a polymer are different, it is termed a *copolymer*. These differences in chemical structure are also illustrated in Figure 1.2, with generic symbols (A, B) for the monomers.

Polymers can be either linear or branched as illustrated in Figure 1.3. The tendency for a polymer to exhibit branching is governed by its synthesis conditions. Keep in mind that the conceptual models of polymer structure illustrated in Figures 1.2 and 1.3 have been highly simplified. For example, it is possible for a copolymer to have a wide range of substructural elements giving rise to an impressive range of possibilities. In industrial practice, polyethylenes, including UHMWPE, are often copolymerized with other monomers (e.g., polypropylene) to achieve improved processing characteristics or to alter the physical and mechanical properties of the polymer. For example, according to ISO 11542, which is the industrial standard for UHMWPE, the polymer can contain a large concentration of copolymer (up to 50%) and still be referred to as UHMWPE. However, most of the UHMWPEs used to fabricate orthopedic implants are homopolymers, and so we will restrict our further discussion to polymers with only a single type of monomer.

The principal feature of a polymer that distinguishes it from other materials, such as metals and ceramics, is its molecular size. In a metallic alloy or ceramic,

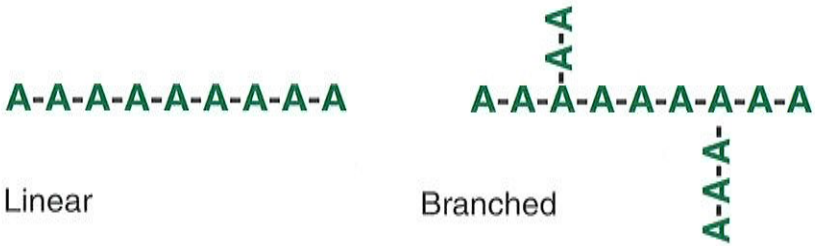


Figure 1.3
Schematics of linear and branched polymer structures.

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the elemental building blocks are individual metal atoms (e.g., Co, Cr, Mo) or relatively small molecules (e.g., metal carbides or oxides). However, in a polymer, the molecular size can comprise more than a 100,000 monomer units, with molecular weights of up to millions of g/mol.

The molecular chain architecture of a polymer also imparts many unique attributes, including temperature dependence and rate dependence. Some of these unique properties are further illustrated in the specific case of UHMWPE in subsequent sections of this chapter. For further background on general polymer concepts, the reader is referred to textbooks by Rodriguez (1989) and Young (1983).

What Is Polyethylene?

Polyethylene is a polymer formed from ethylene (C_2H_4), which is a gas having a molecular weight of 28. The generic chemical formula for polyethylene is $-(C_2H_4)_n-$, where n is the degree of polymerization. A schematic of the chemical structures for ethylene and polyethylene is shown in Figure 1.4.

For UHMWPE, the molecular chain can consist of as many as 200,000 ethylene repeat units. Put another way, the molecular chain of UHMWPE contains up to 400,000 carbon atoms.

There are several kinds of polyethylene (LDPE, LLDPE, HDPE, UHMWPE), which are synthesized with different molecular weights and chain architectures. LDPE and LLDPE refer to low-density polyethylene and linear low-density polyethylene, respectively. These polyethylenes generally have branched and linear chain architectures, respectively, each with a molecular weight of typically less than 50,000 g/mol.

HDPE is a linear polymer with a molecular weight of up to 200,000 g/mol. UHMWPE, in comparison, has a viscosity average molecular weight of up to 6 million g/mol. In fact, the molecular weight is so ultra-high that it cannot be measured directly by conventional means and must instead be inferred by its intrinsic viscosity (IV).

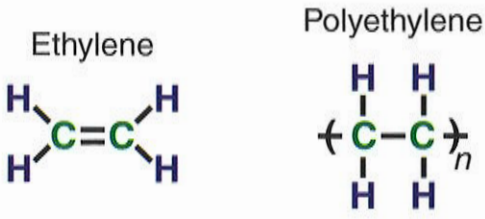


Figure 1.4
Schematic of the chemical structures of ethylene and polyethylene.

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Table 1.1 summarizes the physical and mechanical properties of HDPE and UHMWPE. As shown in Table 1.1, UHMWPE has a higher ultimate strength and impact strength than HDPE.

Perhaps more relevant from a clinical perspective, UHMWPE is significantly more abrasion resistant and wear resistant than HDPE. The following wear data for UHMWPE and HDPE was collected using a contemporary, multidirectional hip simulator (Edidin and Kurtz 2000). Based on hip simulator data, shown in Figure 1.5, the volumetric wear rate for HDPE is 4.3 times greater than that of UHMWPE.

In the early 1960s, UHMWPE was classified as a form of HDPE among members of the polymer industry (Chubberley 1965). Thus, Charnley's earlier references to UHMWPE as HDPE are technically accurate for his time (Charnley 1963), but they have contributed to some confusion over the years as to exactly what kinds of polyethylenes have been used clinically. From a close reading of Charnley's works, it is clear that HDPE is used synonymously with RCH-1000, the trade name for UHMWPE produced by Hoechst in Germany (Charnley 1979). With the exception of a small series of 22 patients who were implanted with silane-crosslinked HDPE at Wrighington (Wroblewski et al. 1996), there is no evidence in the literature that lower molecular weight polyethylenes have been used clinically.

Table 1.1
Typical Average Physical Properties of HDPE, UHMWPE

Property	HDPE	UHMWPE
Molecular weight (10^6 g/mole)	0.05–0.25	2–6
Melting temperature (°C)	130–137	125–138
Poisson's ratio	0.40	0.46
Specific gravity	0.952–0.965	0.932–0.945
Tensile modulus of elasticity* (GPa)	0.4–4.0	0.8–1.6
Tensile yield strength* (MPa)	26–33	21–28
Tensile ultimate strength* (MPa)	22–31	39–48
Tensile ultimate elongation* (%)	10–1200	350–525
Impact strength, Izod* (J/m of notch; 3.175 mm thick specimen)	21–214	>1070 (No Break)
Degree of crystallinity (%)	60–80	39–75

*Testing conducted at 23°C.
From Edidin A.A., and S.M. Kurtz. 2000. The influence of mechanical behavior on the wear of four clinically relevant polymeric biomaterials in a hip simulator. *J Arthroplasty* 15:321–331.

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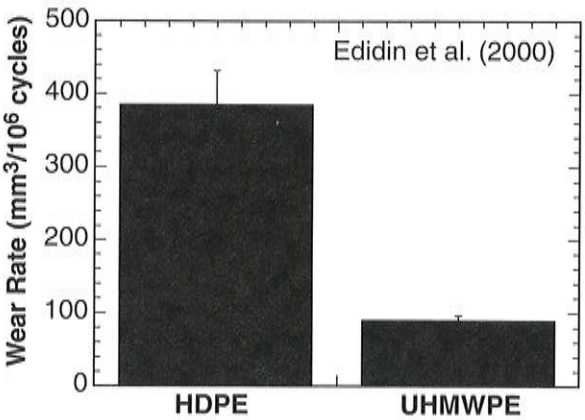


Figure 1.5
Comparison of wear rates of HDPE and UHMWPE in a multidirectional hip simulator. (From Edidin A.A., and S.M. Kurtz. 2000. The influence of mechanical behavior on the wear of four clinically relevant polymeric biomaterials in a hip simulator. *J Arthroplasty* 15:321–331.)

Crystallinity

One can visualize the molecular chain of UHMWPE as a tangled string of spaghetti, more than a kilometer long. Because the chain is not static, but imbued with internal (thermal) energy, the molecular chain can become mobile at elevated temperatures. When cooled below the melt temperature, the molecular chain of polyethylene has the tendency to rotate about the C–C bonds and create chain folds. This chain folding, in turn, enables the molecule to form local ordered, sheetlike regions known as crystalline lamellae. These lamellae are embedded within amorphous (disordered) regions and may communicate with surrounding lamellae by tie molecules. All of these morphological features of UHMWPE are shown schematically in Figure 1.6.

The degree and orientation of crystalline regions within a polyethylene depends on a variety of factors, including its molecular weight, processing conditions, and environmental conditions (such as loading), and will be discussed in later chapters.

The crystalline lamellae are microscopic and invisible to the naked eye. The lamellae diffract visible light, giving UHMWPE a white, opaque appearance at room temperature. At temperatures above the melt temperature of the lamellae, approximately 137°C, UHMWPE becomes translucent. The lamellae are on the order of 10–50 nm in thickness and 10–50 μm in length (Kurtz et al. 1999). The average spacing between lamellae is on the order of 50 nm (Bellare, Schnablegger, and Cohen 1995).

The crystalline morphology of UHMWPE can be visualized using transmission electron microscopy (TEM), which can magnify the polymer by up to

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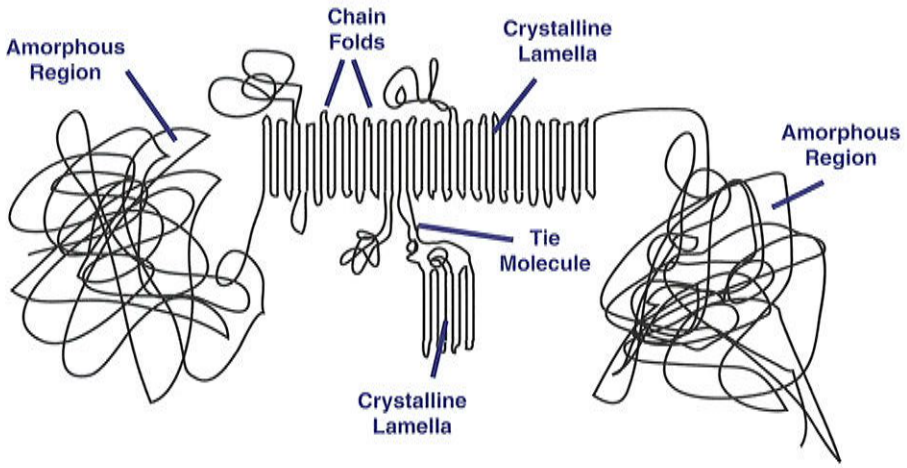


Figure 1.6
Morphological features of UHMWPE.

16,000 times. An ultramicrotomed slice of the polymer is typically stained with uranyl acetate to improve contrast in the TEM. The staining procedure makes the amorphous regions turn gray in the micrograph. The lamellae, which are impervious to the contrast agent, appear as white lines with a dark outline. From the TEM micrograph in Figure 1.7, one can appreciate the composite nature of UHMWPE as an interconnected network of amorphous and crystalline regions.

Thermal Transitions

As already indicated, one of the distinguishing characteristics of polymeric materials is the temperature dependence of their properties. Returning to our conceptual model of an UHMWPE molecule as a mass of incredibly long spaghetti, one must also imagine it to be jiggling and writhing with thermal energy. Generally speaking, many polymers undergo three major thermal transitions: the glass transition temperature (T_g), the melt temperature (T_m), and the flow temperature (T_f).

The glass transition (T_g) is the temperature below which the polymer chains behave like a brittle glass. Below T_g, the polymer chains have insufficient thermal energy to slide past one another, and the only way for the material to respond to mechanical stress is by stretching (or rupture) of the bonds constituting the molecular chain. In UHMWPE, the glass transition occurs at around –160°C.

As we raise the temperature above T_g, the amorphous regions within the polymer gain increased mobility. When the temperature of UHMWPE rises above 60–90°C, the smaller crystallites in the polymer begin to melt. The melting behavior of semicrystalline polymers, including UHMWPE, is typically

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Figure 1.7
TEM micrograph of UHMWPE showing amorphous and crystalline regions (lamellae).

measured using differential scanning calorimetry (DSC). DSC measures the amount of heat needed to increase the temperature of a polymer sample. Some representative DSC data for UHMWPE is shown in Figure 1.8.

The DSC trace for UHMWPE shows two key features. The first feature of the DSC curve is the peak melting temperature (T_m), which occurs at around 137°C and corresponds to the point at which the majority of the crystalline regions have melted. The melt temperature reflects the thickness of the crystals, as well as their perfection. Thicker and more perfect polyethylene crystals will tend to melt at a higher temperature than smaller crystals.

In addition, the area underneath the melting peak is proportional to the crystallinity of the UHMWPE. DSC provides a measure of the total heat energy per unit mass (also referred to as the change in enthalpy, ΔH) required to melt the crystalline regions within the sample. By comparing the change in enthalpy of an UHMWPE sample to that of a perfect 100% crystal, one can calculate the degree of crystallinity of the UHMWPE. Most bulk UHMWPEs are approximately 50–55% crystalline.

As the temperature of a semicrystalline polymer is raised above the melt temperature, it may undergo a flow transition and become liquid. Polyethylenes with a molecular weight of less than 500,000 g/mol can be observed to undergo such a flow transition (T_f). However, when the molecular weight of polyethylene increases above 500,000 g/mol, the entanglement of the

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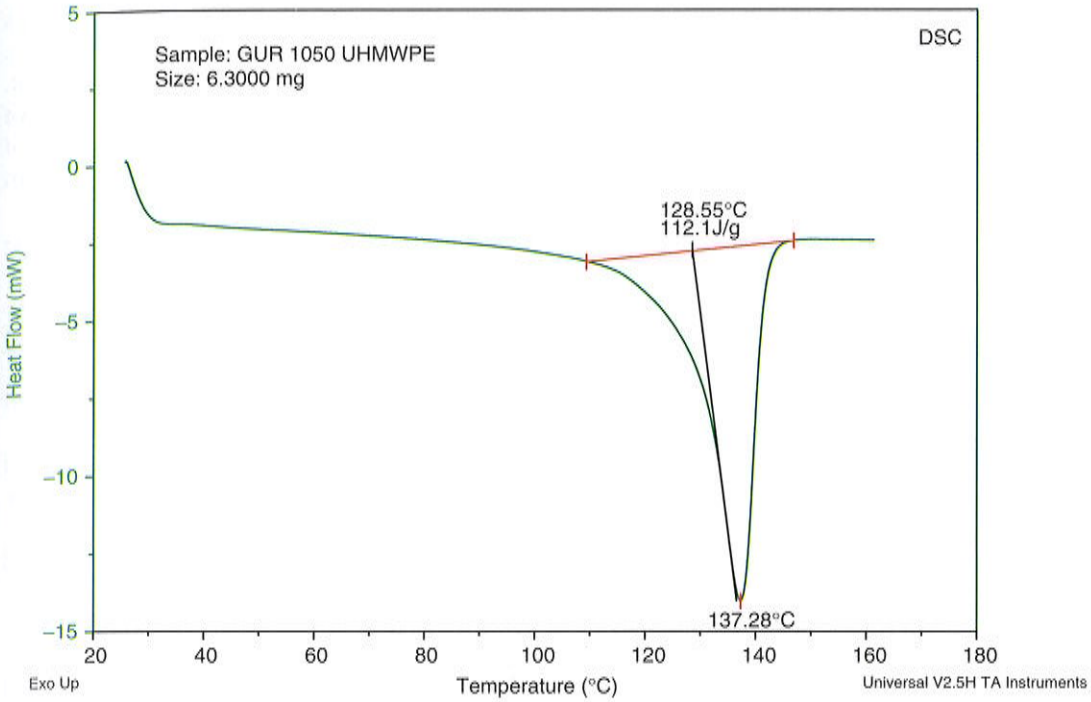


Figure 1.8
DSC trace for UHMWPE.

immense polymer chains prevents it from flowing. UHMWPE does not exhibit a flow transition for this reason.

1.6 Overview of the *Handbook*

This *Handbook* is organized into three main sections. The first section, consisting of three chapters, reviews the basic scientific and engineering foundations for UHMWPE. For example, in Chapter 2, we explain how UHMWPE must be formed into bulk components from the resin powder using extrusion or compression molding techniques. In Chapter 3, we review the techniques associated with sterilization and packaging of UHMWPE implants.

The second part of the *Handbook* is focused on the use of UHMWPE as an orthopedic biomaterial. Chapter 4 reviews the clinical origins of UHMWPE in hip replacement, which was introduced to orthopedics in 1962 by Sir John Charnley. Although several variants of UHMWPE have been investigated since the 1960s, UHMWPE remains the gold standard orthopedic bearing material still widely used today in joint replacements around the world. Chapter 5

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summarizes the clinical performance of UHMWPE hip implants and discusses the patterns of wear and surface damage that occur during implantation. Chapter 6 describes alternatives to conventional UHMWPE in hip replacement. Chapters 7 and 8 relate to the development and clinical performance of UHMWPE in knee replacement. Chapter 9 is devoted to clinical applications of UHMWPE in the shoulder, and Chapter 10 covers the use of UHMWPE in the spine.

The topics outlined in this *Handbook* may be used as a resource in undergraduate, as well as graduate, courses in biomaterials and orthopedic biomechanics. Students in these disciplines can learn a great deal from exposure to the historical development of total joint replacements within the context of UHMWPE. The first two main sections of this book, which cover the fundamentals of UHMWPE and clinical applications in the spine and upper and lower extremities, are intended as a resource for undergraduate instruction.

The third section of this book, which covers more specialized topics related to UHMWPE, is intended for an audience of graduate students and orthopedic researchers. Chapter 11 covers the chemistry of UHMWPE following irradiation, which leads to oxidation and crosslinking of the material. Chapter 12 describes the characterization methods for UHMWPE in the context of regulatory submissions prior to clinical trials. In Chapter 13, we review the development of the small punch test, a miniature specimen mechanical testing technique that has recently been standardized. Chapter 14 describes the micromechanical modeling of conventional and highly crosslinked UHMWPE. The final chapter in this work, Chapter 15, is a compendium of the processing, packaging, and sterilization information for highly crosslinked and thermally treated UHMWPE materials that are currently used in hip and knee arthroplasty.

Understanding basic chemical structure and morphology is an important starting point for appreciating the unique and outstanding properties of UHMWPE. The chapters that follow and describe the processing, as well as the sterilization, of UHMWPE will continue to build on the conceptual foundation established in this introduction.

References

Bellare A., H. Schnablegger, and R.E. Cohen. 1995. A small-angle x-ray scattering study of high-density polyethylene and ultra-high molecular weight polyethylene. *Macromolecules* 17:2325–2333.

Charnley J. 1963. Tissue reaction to the polytetrafluoroethylene. *Lancet* II:1379.

Charnley J. 1979. Low friction principle. In *Low friction arthroplasty of the hip: Theory and practice*. Berlin: Springer-Verlag.

Chubberley A.H. 1965. Ultra-high molecular weight polyethylenes. In *Modern plastics encyclopaedia*. New York: McGraw-Hill.

Edidin A.A., and S.M. Kurtz. 2000. The influence of mechanical behavior on the wear of four clinically relevant polymeric biomaterials in a hip simulator. *J Arthroplasty* 15:321–331.

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Kurtz S.M., O.K. Muratoglu, M. Evans, A.A. Edidin. 1999. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. *Biomaterials* 20:1659–1688.

Rodriguez F. 1989. *Principles of polymer systems*. New York: Hemisphere.

Wroblewski B.M., P.D. Siney, D. Dowson, and S.N. Collins. 1996. Prospective clinical and joint simulator studies of a new total hip arthroplasty using alumina ceramic heads and cross-linked polyethylene cups. *Journal of Bone & Joint Surgery* 78B:280–285.

Young R.J. 1983. *Introduction to polymers*. London: Chapman and Hall.

Chapter 1. Reading Comprehension Questions

1.1. Let A, B, and C be monomers. What is the molecular structure of a linear homopolymer?
a) –A-A-B-A-A-B-A-A-B-
b) –A-B-C-A-B-C-A-B-C-
c) -B-C-C-C-C-C-C-C-C-
d) –B-B-B-B-B-B-B-B-B-
e) –C-A-A-C-A-A-C-A-A-

1.2. Which of the following polymers is NOT synthesized from ethylene?
a) LLDPE
b) PTFE
c) UHMWPE
d) HDPE
e) LDPE

1.3. What is the major difference between HDPE from UHMWPE?
a) Molecular weight
b) Monomer
c) Chemical composition
d) Color
e) All of the above

1.4. What are the crystals in polyethylene made up of?
a) Folded molecular chains
b) Calcium stearate
c) Aluminum tetrachloride
d) Copolymer
e) Branched chain ends

1.5. UHMWPE exhibits which of the following transition temperatures?
a) Glass transition
b) Melting transition
c) Flow transition
d) Glass and melting transitions
e) Glass, melting, and flow transitions

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1.6. What do the tie molecules in UHMWPE interconnect?
a) Molecular chain ends
b) Molecular chain folds
c) Crystalline lamellae
d) Amorphous regions
e) Molecular branching

1.7. What happens to UHMWPE above T_m?
a) The polymer becomes a viscous liquid
b) The polymer becomes brittle and glassy
c) The polymer becomes a gaseous vapor
d) The polymer becomes opaque
e) The polymer becomes translucent

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Chapter 2

From Ethylene Gas to UHMWPE Component: The Process of Producing Orthopedic Implants

Introduction

At a conceptual level, polyethylene consists only of carbon and hydrogen, as was described in the previous chapter. However, if the discussion of polyethylene is to proceed from ideal abstractions to actual physical implants, three "real world" steps need to occur. First, the ultra-high molecular weight polyethylene (UHMWPE) must be polymerized from ethylene gas. Second, the polymerized UHMWPE, in the form of resin powder, needs to be consolidated into a sheet, rod, or near-net shaped implant (Figure 2.1). Finally, in most instances, the UHMWPE implant needs to be machined into its final shape (Figure 2.1). A small subset of implants are consolidated into their final form directly, in a process known as direct compression molding (DCM), without need of additional machining.

Each of these three principal steps produces a subtle alteration of the properties of UHMWPE. In some cases, such as machining, the change in the material may occur only in the topography and appearance of the surface. On the other hand, changes in the polymerization and conversion of the UHMWPE can impact the physical and mechanical properties of the entire implant.

Because many of the details used in the polymerization, conversion, and machining of UHMWPE are proprietary, very little is written in the public domain literature about the techniques used to make actual implants. The little that has been written about implant production can be confusing to the

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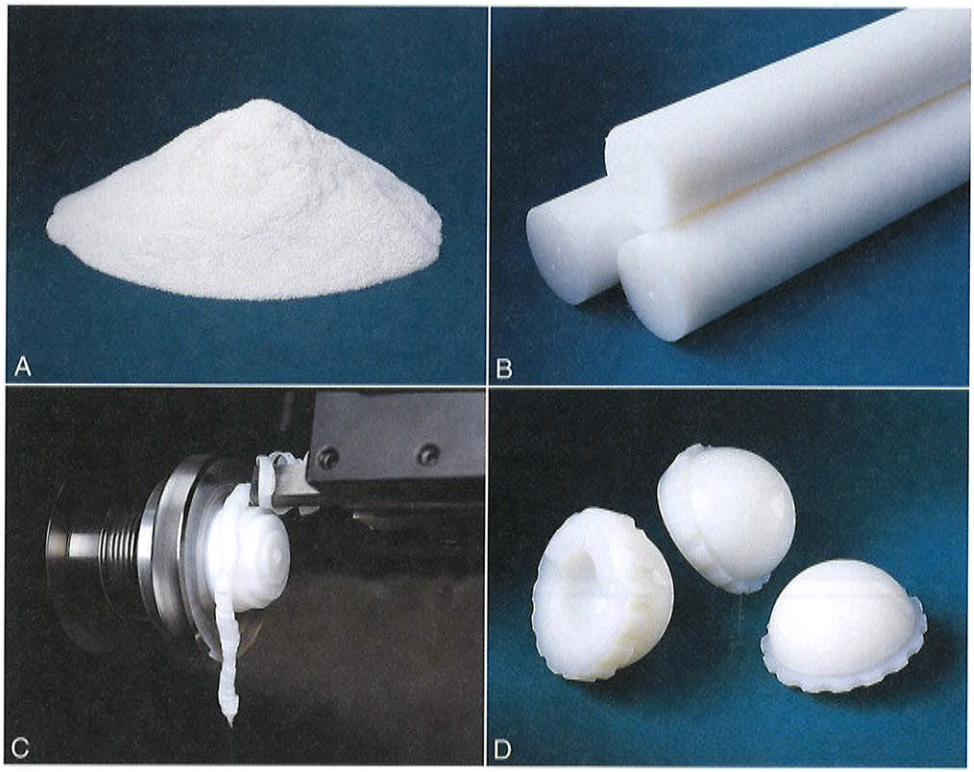


Figure 2.1
Typical processing steps in the manufacture of UHMWPE implants, starting with the resin powder (**A**). (**B**) Semifinished rods that have been consolidated from the resin powder. (**C**) Machining of the UHMWPE rods on a lathe. (**D**) UHMWPE acetabular components after machining. (Pictures provided courtesy of David Schroeder [Biomet, Warsaw, IN].)

uninitiated because of the abundance of trade names, which evolve over time. Not only do industrial trade names change over time, but the actual processing techniques have also improved. Surgeons and researchers are strongly cautioned against overgeneralizing about the properties or techniques of any single resin or process, which has likely changed over the past 40 years.

Polymerization: From Ethylene Gas to UHMWPE Powder

The polymerization of UHMWPE was commercialized by Ruhrchemie AG, based in northern Germany, during the 1950s. Ruhrchemie AG itself evolved in 1928 with the mission of developing useful chemicals from coal (carbon); its shareholders consisted of 28 coal mining companies. In 1953, chemists from

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the nearby Max-Plank Institute approached scientists at Ruhrchemie AG in Oberhausen, Germany, with a brown, wet (not fully dried) mass that they claimed was a new form of polyethylene, produced in a new low-pressure process. Convinced of the commercial utility of such a material (the dangers of high-pressure polymerization, such as in the production of low-density polyethylene (LDPE), were widely appreciated), development on UHMWPE began shortly thereafter at Ruhrchemie AG. In 1955, the first commercial polymerization of UHMWPE began, and during that same year, the material was first introduced at the K55, a polymer trade show.

Since the 1950s, the UHMWPE powders have been produced by Ruhrchemie (currently known as Ticona) using the Ziegler process, which has been described by Birnkraut (1991). The main ingredients for producing UHMWPE are ethylene (a reactive gas), hydrogen and titanium tetra chloride (the catalyst). The polymerization takes place in a solvent used for mass and heat transfer. The ingredients require that the polymerization be conducted in specialized production plants capable of handling these volatile and potentially dangerous chemicals. The last ingredient (catalyst) has been improved consistently since the 1950s because it is the key to producing white UHMWPE powder with reduced impurities.

The requirements for medical grade UHMWPE powder are specified in the American Society for Testing and Materials (ASTM) standard F648 and ISO standard 5834-1. In the standards, medical grade resins are described as Types 1, 2, or 3, depending on their molecular weight and producer (Table 2.1). The trace impurities of titanium, aluminum, and chlorine are residuals from the catalyst, whereas the trace levels of calcium, as well as the ash content, depend on the storage and handling of the powder after polymerization.

Table 2.1
Requirements for Medical Grade UHMWPE Powders (per ASTM F648 and ISO 5834-1)

Property	Requirements	
Resin type	Types 1–2	Type 3
Trade name	GUR 1020 & 1050	1900H
Producer	Ticona, Inc.	Basell polyolefins (now discontinued)
Ash, mg/kg, (maximum)	150	300
Titanium, ppm, (maximum)	40	150
Aluminum, ppm, (maximum)	40	100
Calcium, ppm, (maximum)	50	50
Chlorine, ppm, (maximum)	20	90

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Currently Ticona (Oberhausen, Germany) produces a Type 1 and Type 2 resin with the trade names of GUR 1020 and 1050, respectively. Before 2002, Basell Polyolefins (Wilmington, DE) produced a Type 3 resin with the 1900 trade name. This resin was discontinued in January 2002 and is no longer produced. Two orthopedic manufacturers have maintained large stockpiles of this resin. Therefore, orthopedic implants will continue to be fabricated from this resin, at least in the near future.

The orthopedics literature contains numerous references to different trade names for UHMWPE, which fall into two categories: 1) GUR resins currently produced by Ticona and 2) the 1900 resins, previously produced by Basell. The UHMWPE grades currently used in the orthopedic industry are summarized in Table 2.2.

GUR Resins

Ticona (formerly known as Hoechst, and before that, as Ruhrchemie AG) currently supplies 800 tons of premium grade UHMWPE per year for orthopedic applications. This is less than 2% of Ticona's overall UHMWPE production. Resin is currently manufactured in Bishop, TX, and Oberhausen, Germany. The resin grades produced at Bishop and Oberhausen use the same catalyst technology and undergo similar resin synthesis processes. When tested in accordance with ASTM F648 and ISO 5834, the physical and mechanical properties of the Bishop and Oberhausen resins are indistinguishable. Ticona uses the designation GUR for its UHMWPE grades worldwide; the acronym GUR stands for "Granular," "UHMWPE," and "Ruhrchemie."

Hoechst changed its resin nomenclature between 1992 and 1998. Resins distributed to both the general and orthopedic marketplaces before 1992 were designated as, for example, GUR 415, and GUR 412 in the United States, or CHIRULEN® P in Europe. In October 1992, a fourth digit was added to all general and orthopedic products to allow inclusion of additional resins to the product lines. For example, GUR 415 became GUR 4150. In 1994, after the

Table 2.2
Nomenclature of Ticona and Basell UHMWPE Resins. The Average Molecular Weight is Calculated Based on Intrinsic Viscosity

Resin designation	Producer	Average molecular weight (10^6 g/mol)	Calcium stearate added?
GUR 1020	Ticona	3.5	No
GUR 1050	Ticona	5.5–6	No
1900H*	Basell	>4.9	No

*Note: Production of this resin was discontinued in 2002.

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sale of the CHIRULEN trade name, Hoechst in Europe decided to exclusively designate all resins for the surgical implant market with a first digit of "1." By comparison, Hoechst in North America renamed GUR 4150 as GUR 4150HP (to designate High Purity) for this application in August 1993. In 1998, all of the nomenclature was consolidated with the availability of four grades for the worldwide orthopedic market—GUR 1150, 1050, 1120, and 1020 resins (Table 2.2).

The first digit of the grade name was originally the loose bulk density of the resin, i.e., the weight measurement of a fixed volume of loose, unconsolidated powder; the "4" corresponded to a bulk density of more than 400 g/l for standard grades. The second digit indicates the presence (1) or absence (0) of calcium stearate, whereas the third digit is correlated to the average molecular weight of the resin. The fourth digit is a Hoechst internal code designation. Most recently, in 2002, Ticona discontinued the production of GUR 1120 and 1150, which contained added calcium stearate.

1900 Resins

Although Basell, prior to 2002, produced six grades of 1900 resin, only one of these grades (1900H) is currently used in orthopedic applications (Table 2.2). Since its introduction by the Hercules Powder Company (Wilmington, DE), 1900 resin has been through transitions in nomenclature and production. During the 1960s, Hercules produced several grades of Hi-Fax 1900 UHMWPE with molecular weights ranging from 2 million to 4 million (Chubberley 1965). In 1983 Hercules formed a joint venture with Montedison in Italy to become Himont. In April 1995, Montedison and Shell Oil (Netherlands) formed Montell Polyolefins; the company was merged into BASF and Shell, forming Basell Polyolefins in 2001. In January 2002, Basell divested itself of its UHMWPE production facilities and sold its technology to Polialden, a Brazilian UHMWPE manufacturer.

The resin designation of 1900 has stayed the same through the past three decades of transitions while Montell changed the manufacturing facilities. Over this time, three different reactors were used to produce the different grades of 1900. Originally the A-line reactor was used, but in 1989–1990 Himont began producing the resin on their F-line. The latter line was a semicontinuous process as compared with the batch processing used earlier. In 1996–1997 the F-line was replaced with the G-line. In early 2002, Basell dismantled the G-line production facility. The current owner of the 1900 resin technology, Polialden, has not yet announced whether they intend to resume production for orthopedic use in Brazil.

Molecular Weight

The mechanical behavior of UHMWPE is related to its average molecular weight, which is routinely inferred from intrinsic viscosity (IV) measurements

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(Eyerer, Frank, and Jin 1985, Li and Burstein 1994). There are two commonly used methods for calculating the viscosity average molecular weight (M_v) for UHMWPE based on the IV using the Mark-Houwink equation:

1. ASTM D4020-00: $M_v = 53{,}700\ IV^{1.37}$
2. Margolies equation, used outside North America: $M_v = 53{,}700\ IV^{1.49}$

In the previous equations, M_v has units of g/mol and IV has units of dL/g. Alternative methods for molecular weight characterization of UHMWPE include sequential extraction (Kusy and Whitley 1986) and gel permeation chromatography (GPC), a type of size exclusion chromatography (Wagner and Dillon 1988).

The IV of UHMWPE is related to the bulk impact strength and abrasive wear resistance after conversion to bulk form, although the relationships are nonlinear. The maximum impact strength of both Ticona and Basell is found between 16 and 20 IV, which is the equivalent to a molecular weight range of 2.4 million to 3.3 million using the ASTM calculation for molecular weight. As the IV increases, abrasive wear resistance increases, as measured by sand slurry testing, reaching a plateau for IV greater than 20.

Molecular weight also influences the static fracture response as well as the mechanical behavior of UHMWPE at large strains (Kurtz et al. 1998). For example, beyond the polymer yield point, the hardening or cold drawing portion behavior in uniaxial tension is sensitive to the molecular weight. Figure 2.2 illustrates the true-stress strain curve in uniaxial tension (room temperature, 30 mm/min) for two grades of UHMWPE, in comparison with high-density polyethylene (HDPE).

Under biaxial drawing conditions of the small punch test (Edidin and Kurtz 2001), the large-deformation mechanical behavior of polyethylene also

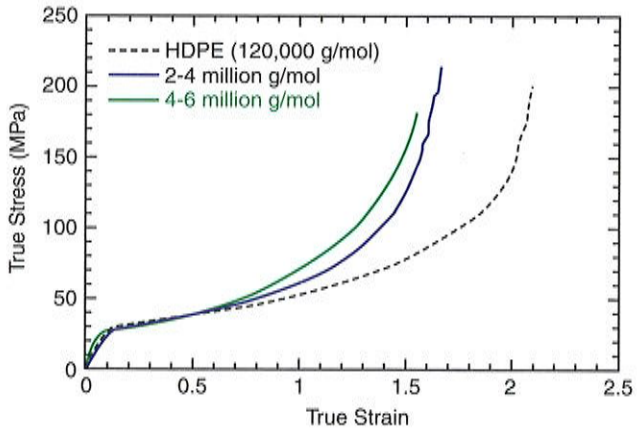


Figure 2.2

The true-stress strain behavior in uniaxial tension (room temperature, 30 mm/min) for two grades of UHMWPE, in comparison with HDPE.

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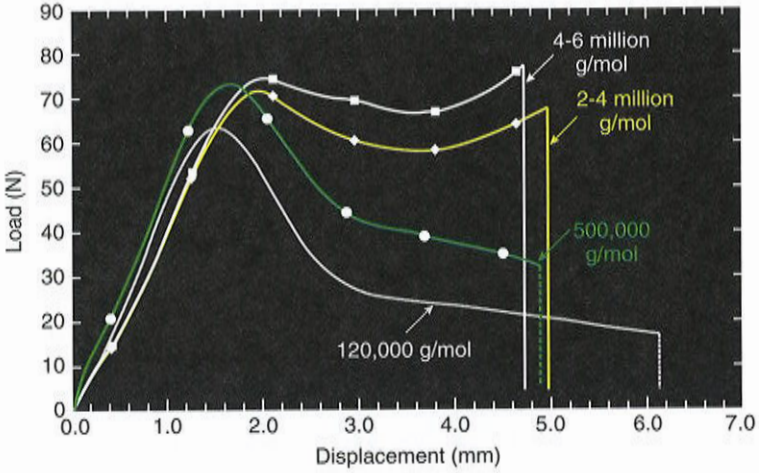


Figure 2.3
Representative small punch test data conducted at room temperature at a rate of 0.5 mm/min.

displays strong molecular weight dependence. Representative small punch test data, shown in Figure 2.3, were conducted at room temperature at a rate of 0.5 mm/min.

GUR Versus 1900 Resin

Variations between the material properties of converted GUR and 1900 resins have been explained by differences in the average resin particle size, the size distribution, and morphology of the resin particles (Gul 1997, Han et al. 1981). Ticona resins have a mean particle size of approximately 140 μm (Gul 1997, Han et al. 1981), whereas the mean particle size of 1900 resin is approximately 300 μm (Han et al. 1981). The distribution of particle sizes also varies between Ticona and Basell resins. When studied under a scanning electron microscope, GUR and 1900 resin powders consist of numerous spheroidal particles (Gul 1997, Han et al. 1981). The scanning electron micrographs seen in Figure 2.4 (provided courtesy of Rizwan Gul [1997]) illustrate the subtle differences in nascent particle morphology between Basell and Ticona resins, which are likely related to the catalyst package and polymerization conditions (Birnkraut 1991).

The most notable finding from studies of powder morphology is that the Ticona resins are characterized by a fine network of submicron-sized fibrils that interconnect the microscopic spheroids. The fibrils are illustrated in the scanning electron microscopy (SEM) micrograph in Figure 2.5 (provided courtesy of Rizwan Gul [1997]).

There is some evidence that Basell resins have a different molecular weight distribution than the Ticona resins (Gul 1997). For example, depending on the

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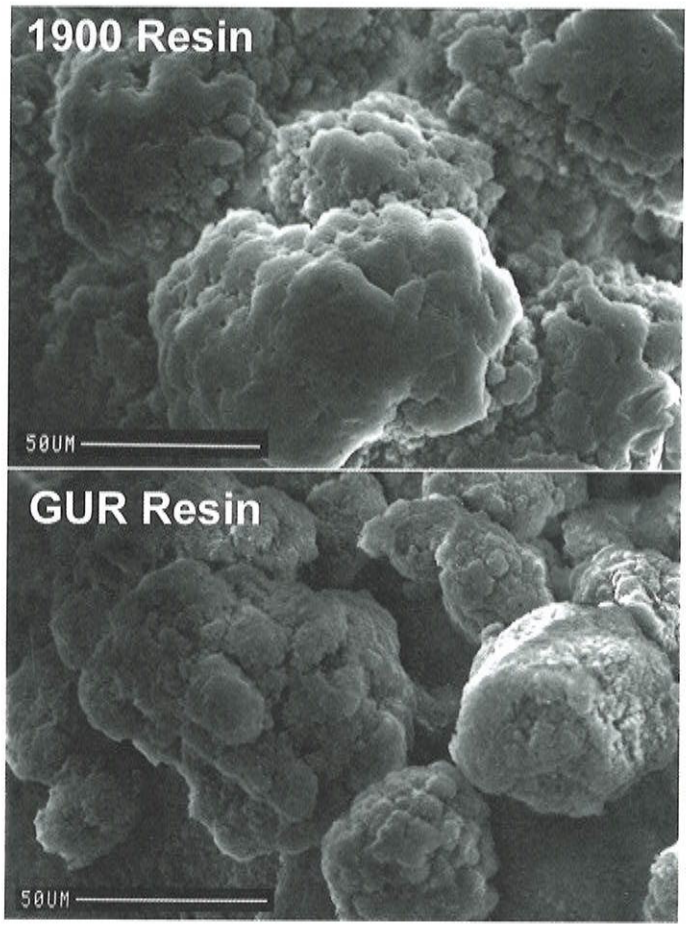


Figure 2.4
The scanning electron micrographs illustrate the subtle differences in nascent particle morphology between Basell and Ticona resins.

processing conditions, Basell 1900 exhibits spherulitic crystalline morphology (Gul 1997, Weightman and Light 1985), which is typically associated with slightly lower molecular weight polyethylenes (Voigt-Martin, Fisher, and Mandelkern 1980). Spherulites are not observed in Ticona resins, which have a lamellar crystalline morphology (Goldman et al. 1996, Gul 1997, Pruitt and Bailey 1998). Differences in the molecular weight distribution between the Basell- and Ticona-produced resins may account for the variation in impact strength observed experimentally at the same average molecular weight. However, despite clues in the literature, the differences in molecular weight distribution between Basell and Ticona resins have yet to be explicitly quantified.

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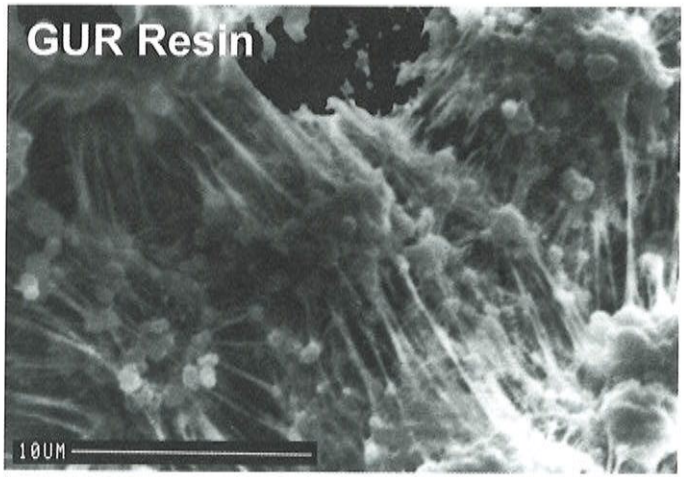


Figure 2.5
SEM image of submicron size fibrils in GUR resins.

Calcium Stearate

Calcium stearate has been used by Hoechst since 1955 and by Montell since the late 1960s. The additive acts as a scavenger for residual catalyst components that can potentially corrode conversion equipment; calcium stearate also acts as a lubricant and a release agent (Eyerer et al. 1990). The catalyst used by Ticona today has a higher activity than the one originally used for UHMWPE production. Thus, a larger quantity of UHMWPE can be synthesized with the same amount of catalyst, resulting in a lower residual catalyst concentration (Birnkraut 1991). The trace element level of calcium in UHMWPE is directly proportional to the addition of calcium stearate, which is currently certified as food grade (Stein 1997). When calcium stearate is added to any UHMWPE resin, regardless of the manufacturer or catalyst technology used, the polymer particles are surface coated by the calcium stearate.

During the 1980s, the influence of calcium stearate on the properties and performance of UHMWPE total joint replacements was considered a controversial issue (Kurtz et al. 1999). In several studies, the presence of trace calcium levels in UHMWPE has been associated with fusion defects and oxidation of UHMWPE (Biomet 1995, Blunn et al. 1997, Eyerer et al. 1990, Gsell, King, and Swarts 1997, Hamilton, Wang, and Sung 1996, Schmidt and Hamilton 1996, Swarts et al. 1996, Walker, Blunn, and Lilley 1996, Wrona et al. 1994). Using high-resolution synchrotron infrared spectroscopy, Muratoglu and colleagues (1997) resolved the molecular vibrations associated with calcium stearate in the grain boundary layers of fusion defects in GUR 4150HP; examination of converted GUR 4050 and HIMONT 1900, in contrast, showed no evidence of calcium stearate. In an accelerated aging study by Swarts and colleagues (1996),

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GUR 4150HP exhibited more oxidation than reduced-calcium stearate resins (GUR 4050 and Montell 1900H).

However, the mere presence of calcium stearate does not automatically imply poor consolidation and decreased fracture resistance in UHMWPE. For example, using the J-integral method, Baldini and colleagues (1997) reported that the fracture resistance of GUR 1020 and 1120 were "comparable." Lykins and Evans (1995) have suggested that fusion defects may result from inappropriate control of processing variables (e.g., temperature, pressure, time, heating rate) during conversion of resin to stock material. Thus, it remains to be established whether calcium stearate plays a role in the mechanical behavior of well-consolidated UHMWPE except at sufficiently high enough concentrations to interfere with the sintering of the powder.

Thus, research conducted during the 1990s indicated that calcium stearate may be present at the boundaries of fusion defects in UHMWPE, and that fusion defects may in turn deleteriously affect the fatigue and fracture behavior of UHMWPE. However, in the absence of fusion defects, the deleterious effects of trace levels of calcium stearate were not conclusively established. Furthermore, polymerization and processing technology had by the late 1990s evolved to the point that the additive was no longer necessary. Consequently, orthopedic manufacturers began switching to UHMWPE resins without added calcium stearate (e.g., GUR 1020 and 1050). By 2002, demand for the calcium stearate–containing resins (GUR 1120 and 1150) dropped to the point that Ticona discontinued its production.

Conversion: From UHMWPE Powder to Consolidated Form

UHMWPE is produced as powder and must be consolidated under elevated temperatures and pressures because of its high melt viscosity. As already discussed in Chapter 1, UHMWPE does not flow like lower molecular weight polyethylenes when raised above its melt temperature. For this reason, many thermoplastic processing techniques, such as injection molding, screw extrusion, or blow molding, are not practical for UHMWPE. Instead, semifinished UHMWPE is typically produced by compression molding and ram extrusion.

The process of consolidation in UHMWPE requires the proper combination of temperature, pressure, and time. The precise combinations of these variables used to produce commercially available molded and extruded stock materials remain proprietary, but the scientific principles underlying consolidation of UHMWPE are generally well understood (Barnetson and Hornsby 1995, Bastiaansen, Meyer, and Lemstra 1990, Bellare and Cohen 1996, Chen, Ellis, and Crugnola 1981, Farrar and Brain 1997, Gul 1997, Halldin and Kamel 1977a, Halldin and Kamel 1977b, Han et al. 1981, McKenna, Crissman, and Khoury 1981, Olley et al. 1999, Shenoy and Saini 1985, Truss et al. 1980, Wang, Li, and Salovey 1988, Zachariades 1985). The governing mechanism of consolidation is self-diffusion, whereby the UHMWPE chains (or chain segments) in adjacent resin particles intermingle at a molecular level. The kinetics of intergranular

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diffusion are promoted by close proximity of the interfaces (at elevated pressures) and thermally activated mobility of the polymer chains (at elevated temperatures). As a diffusion-limited process, consolidation of UHMWPE requires sufficient time at elevated temperature and pressure for the molecular chains to migrate across grain boundaries.

Consolidated UHMWPE retains a memory of its prior granular structure, which is especially evident when calcium stearate is added to the resin (Bastiaansen, Meyer, and Lemstra 1990, Farrar and Brain 1997, Gul 1997, Olley et al. 1999). The ultrastructure of UHMWPE may be visualized by either optical or SEM, but special preparation methods are needed in either case. A standard technique, described in ASTM F648, involves microtoming thin films and observing them under optical microscopy, preferably under dark field conditions (Halldin and Kamel 1977a). However, in today's calcium-stearate free-resins, the presence of grain boundaries in well-consolidated material is usually difficult to detect, as illustrated in Figure 2.6, the following optical micrograph of a 100 µm–thick section of GUR 1020 (provided courtesy of Rolf Kaldeweier, Ticona, Inc.).

Grain boundaries can also be visualized by freezing an UHMWPE sample in liquid nitrogen and then fracturing the sample while frozen (Gul 1997). Etching of fracture surfaces can further highlight the intergranular regions, allowing for visualization of the UHMWPE ultrastructure (Olley et al. 1999). SEM is then used to inspect the surface of the freeze-fractured or etched UHMWPE surfaces.

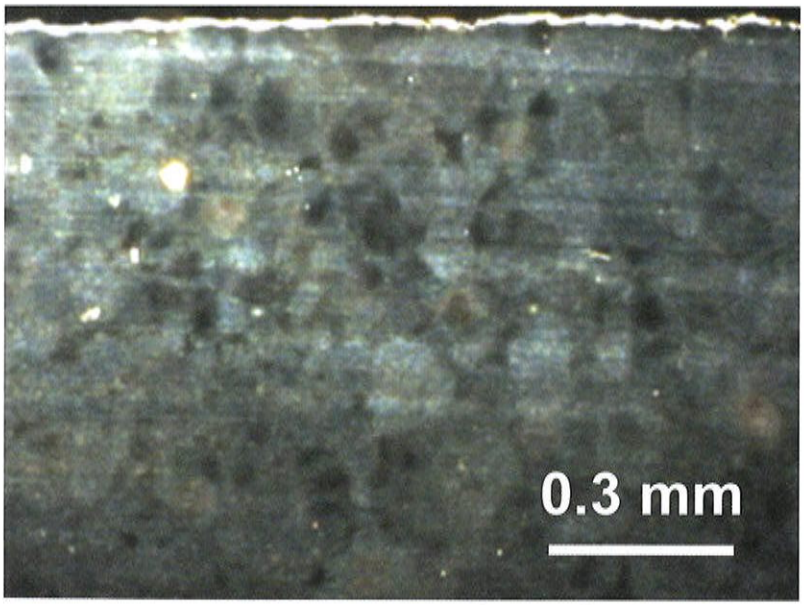


Figure 2.6
An optical micrograph of a 100 µm–thick section of GUR 1020.

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In contrast with grain boundaries, which reflect the normal ultrastructure of UHMWPE, consolidation defects may arise when the proper combination of pressure, temperature, and time are not used (Lykins and Evans 1995). More typically, consolidation defects represent a single resin particle, or a highly localized region, that has not fully fused with its neighbors. A standard technique (specified in ASTM F648), involving optical microscopy of thin sections, has been developed to quantify the presence of fusion defects in UHMWPE. Interinstitutional studies are currently progressing under the auspices of ASTM to quantify the repeatability and reproducibility of the standard inspection technique in contemporary calcium-stearate–free resins. Nondestructive methods, including laser candling and ultrasound, are also used in industry for inspection of medical grade UHMWPE, but the use of these techniques has not been standardized.

Compression Molding of UHMWPE

Historically, the UHMWPE powder has been converted by compression molding since the 1950s, because the industries in the area around Ruhrchemie already had experience with this processing technique. At first, the semi-finished material was distributed under the trade name RCH 1000/Hostalen GUR 412. During the 1970s, the compression-molded UHMWPE was manufactured and distributed by Ruhrchemie/Hoechst and later distributed by the company Europlast specifically for orthopedic applications under the trade name CHIRULEN, which denoted that the material was produced in Germany by a dedicated press using established processing parameters. Thus, references in the orthopedic literature to RCH 1000 and CHIRULEN apply to compression-molded UHMWPE, which was similar to contemporary GUR 1020. Note, however, that GUR 412 would have contained calcium stearate, whereas GUR 1020 would not.

Today, compression-molded sheets of GUR 1020 and 1050 are produced commercially by two companies (Perplas Medical and Poly Hi Solidur Meditech). Ticona stopped producing compression-molded UHMWPE in 1994. Perplas's molding facility is in England, whereas Poly Hi Solidur produces medical grade UHMWPE sheets in the United States and in Germany.

An example of a compression molding press, currently installed at Poly Hi Solidur Meditech in Vreden, Germany, is shown in Figure 2.7. This particular press, originally designed by Hoechst in the 1970s for production of CHIRULEN, molds two 1 m × 2 m sheets in a single press cycle. One UHMWPE sheet is pressed between the upper and middle platens, and the second is produced between the middle and lower platens. The platens are oil heated and hydraulically actuated from below. The heating and loading systems are all computer controlled. Finally, the entire press is contained in a clean room, to reduce the introduction of extraneous matter into the sheet.

Depending on the size of a press, the UHMWPE sheet may range in size between 1 m × 2 m (shown in the photo) to 2 m × 4 m, with thicknesses of 30 mm to 80 mm. However, the facilities necessary to mold a 2 m × 4 m sheet of UHMWPE are considerably larger than that shown in the photo. The UHMW

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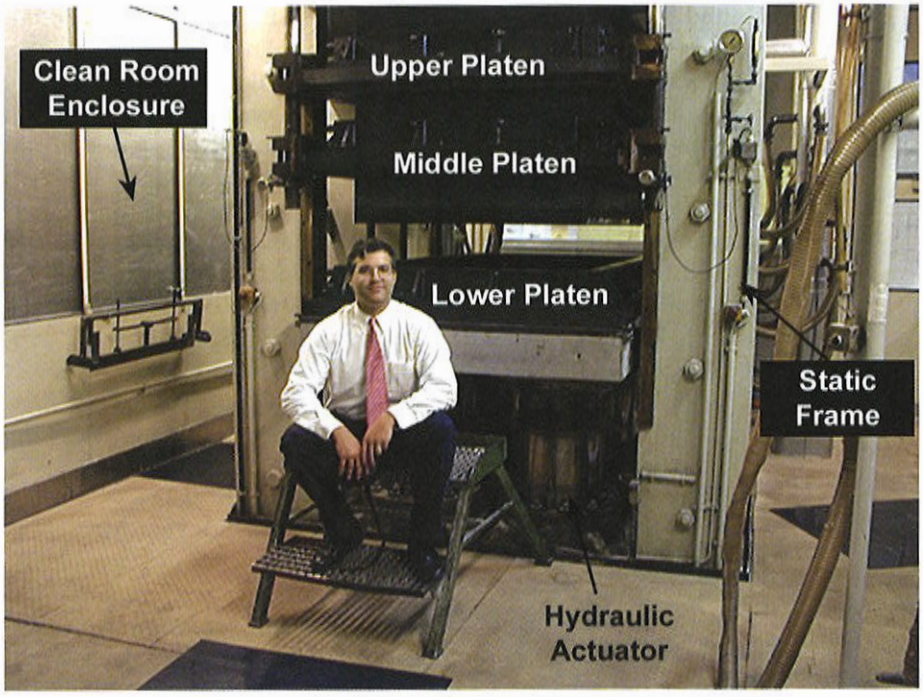


Figure 2.7
Compression molding press (along with the author, for scale) for production of 1 m × 2 m sheets of UHMWPE. This press is located at Poly Hi Solidur Meditech in Vreden, Germany, and was originally used by Ticona in the production of Chirulen sheets of UHMWPE. The press is still used today in the production of medical grade UHMWPE.

operated by Perplas Medical, for example, is over three stories tall and enclosed within its own clean room structure.

Because of the relatively low thermal conductivity of UHMWPE, the duration of the molding cycle will depend on the particular geometry of the press and the size of the sheet to be produced, but the processing time can last up to 24 hours. The long molding times are necessary to maintain the slow, uniform heating and cooling rates throughout the entire sheet during the molding process.

After molding, the sheet is typically turned into rods or other preform shapes to facilitate subsequent machining operations by orthopedic manufacturers. Thus, the final shape of UHMWPE stock material today is not necessarily dictated by the conversion method.

Ram Extrusion of UHMWPE

In contrast with compression molding, which originated in Germany in the 1950s, ram extrusion of UHMWPE was developed by converters in the

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United States during the 1970s. Historically, a wide range of UHMWPE resins have been extruded since the seventies. From the early 1970s to early 1980s, ram extruded Hifax 1900 resin from Hercules Powder Company (Wilmington, DE) was commonly supplied to bulk form converters. In the early 1960s Hoechst's GUR 412 resin was made available to converters. Although GUR 412 tended to have a lower extraneous particle count than 1900, it was also more difficult to process using ram extrusion because of its lower average molecular weight and lower melt viscosity. In the mid 1980s, converters began ram extruding using the higher average molecular weight Hoechst GUR 415 resin, which also had a lower extraneous particle count relative to 1900 and was easier to extrude than GUR 412. During the 1980s and early 1990s, extruded rods of GUR 412, 415, and (more rarely) 1900 CM (a calcium-stearate–containing grade of 1900 resin) were all used in orthopedics. Thus, it is difficult to generalize about the resin types used in implants without tracing the lot numbers used by a particular manufacturer.

Today only a few converters supply medical grade, GUR 1020 and 1050 ram extruded UHMWPE to the orthopedic industry. Medical grade extrusion facilities for Poly Hi Solidur and Westlake Plastics are based in the United States, whereas Perplas Medical's medical grade extrusion is in England.

Like compression molding facilities, a medical grade extruder is typically maintained in a clean room environment to reduce the introduction of extraneous matter into the UHMWPE. The generic schematic of a ram extruder is illustrated in Figure 2.8 (the clean room is not shown).

UHMWPE powder is fed continuously into an extruder. The extruder itself consists essentially of a hopper that allows powder to enter a heated receiving chamber, a horizontal reciprocating ram, a heated die, and an outlet. Within the extruder, the UHMWPE is maintained under pressure by the ram, as well as by the back pressure of the molten UHMWPE. The back pressure is caused by frictional forces of the molten resin against the heated die wall surface as it is

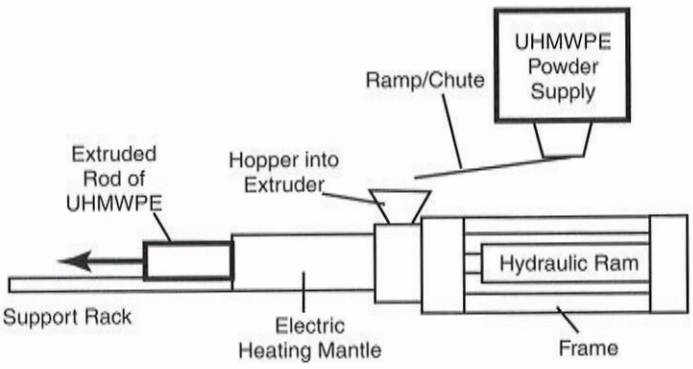


Figure 2.8
Schematic of a ram extruder.

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forced horizontally through the outlet. Beyond the outlet, the rod of UHMWPE is slowly cooled in a series of electric heating mantles.

A wide range of rod diameters is achievable (up to 12 inches in diameter) using extrusion, but the rate of production depends on the rod size because of the increased cooling times needed with the larger rod diameters. Rod sizes ranging from 20 to 80 mm in diameter are most often used in orthopedic applications. Typical production rates are on the order of millimeter per minute.

Hot Isostatic Pressing of ArCom™ UHMWPE

A third conversion method, known as hot isostatic pressing (HIPing), is used by one orthopedic manufacturer (Biomet, Warsaw, IN) for conversion of resin to stock material (Gul 1997). This multistep conversion process, referred to as ArCom™ by the manufacturer, begins with the manufacture of a cylindrical compact through cold isostatic pressing, which expels most of the air (Figure 2.9). Subsequently, the compacted green rods are sintered in a HIP furnace in an argon-filled pouch to prevent degradation of the UHMWPE (Figure 2.9). The resulting ArCom rod stock is essentially isotropic as a result of the hydrostatic sintering process and may be considered a compression-molded form of the resin. Finished implants are then made from the iso-molded rod stock by either turning or milling operations (Biomet 1997), as illustrated in Figure 2.1.

Direct Compression Molding of UHMWPE

In DCM, sometimes also called net shape compression molding, the manufacturer of the polyethylene insert effectively converts the resin to a finished or semifinished part using individual molds. One advantage of DCM is the extremely smooth surface finish obtained with a complete absence of machining marks at the articulating surface. In addition, higher processing pressures may be attained, if desired, because the projected surface area of each individual part mold is relatively small compared with the area of large molds used to compression mold sheets.

DCM has been used for more than 20 years to produce tibial and acetabular inserts. Historically, the process may have been adopted because the cutting and milling machinery of the day was not numerically controlled and thus less able to accurately produce complicated curves as required to make knee inserts. The physical and mechanical properties of the finished product can be tailored to some degree by varying the DCM cycle, as detailed by Chen, Truss, and others (Han et al. 1981, Truss et al. 1980, Chen, Ellis, and Crugnola 1981). DCM can also be used to produce UHMWPE with properties indistinguishable from stock material produced by closely monitored conversion of compression-molded sheet and extruded rod.

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Figure 2.9

Steps in the processing of ArCom UHMWPE (Biomet, Warsaw, IN). (**A**) Resin powder is first poured into a polymeric can with a compressible lid. (**B**) The can is inserted into a cold isostatic press for compaction of the powder. (**C**) Cold pressed ("green") rod of UHMWPE after cold compaction. (**D**) The green rod is sealed in an Argon-filled foil pouch. (**E**) The foil-wrapped green rods are loaded in a metallic mesh rack and lowered into a hot isostatic press. (**F**) The foil-wrapped rod of consolidated UHMWPE after HIPing. The foil is peeled off the rod and machined into components as shown in Figure 2.1. (Pictures provided courtesy of David Schroeder, Biomet, Inc.)

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Overall, the literature suggests that the DCM process can produce a specimen or implant with mechanical properties similar to those exhibited by high-quality bulk converted UHMWPE stock. The variations in final properties seen as functions of temperature, pressure, density, and cooling rate would presumably affect the production of bulk converted sheet and rod. However, bulk conversion needs to be performed much less often to convert a given mass of resin, and thus issues of monitoring and maintaining quality need to be performed less often as well. From a manufacturability standpoint, the difficulties associated with process control of DCM has led most implant producers to obtain bulk converted sheet or rod.

ArCom

ArCom is the trade name of a proprietary conversion process, which denotes that the resin has been compression molded in the presence of argon (Biomet, Warsaw, IN). ArCom is produced by HIPing as well as by DCM.

The type of resins used with ArCom are summarized in Table 2.3. Both 1900H and GUR resins have been fabricated using the ArCom iso-molding process. Between 1993 and 2002, iso-molded ArCom was produced with 1900H resin. In 2002, after Basell discontinued the production of 1900 resin, Biomet switched production of iso-molded rod stock to GUR resins produced by Ticona (Table 2.3). On the other hand, Biomet has stockpiled sufficient 1900H resin to continue production of direct compression-molded ArCom for the foreseeable future (Table 2.3).

Properties of Extruded Versus Molded UHMWPE

As might be expected from our previous discussion of compression molding and extrusion, the conversion method could have an effect on the properties of UHMWPE. In practice, however, the differences between extrusion and

Table 2.3
Summary of Conversion Methods and Resins Used in the Production of ArCom During Both Historical and Contemporary Time Frames

ArCom	Historical	Contemporary
Conversion method	UHMWPE resin	UHMWPE resin
	(1993–2002)	(2002–Present)
Isostatically molding	1900H	GUR 1050
DCM	1900H	1900H*

*This resin continues to be used because it has been stockpiled by the manufacturer.

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Table 2.4
Breakdown of 680 Individual UHMWPE Lots Compared in ASTM Survey

	GUR 1020 (Type 1)	GUR 1050 (Type 2)	Total
Ram extruded	113	218	331
Compression molded	186	163	349
Total	299	381	680

compression molding are slight in the hands of a skilled converter. In 2001, a survey was conducted by the author under the auspices of ASTM to evaluate the variation in physical and mechanical properties of UHMWPE as a function of resin and conversion method. Three commercial suppliers provided physical and mechanical property data collected during certification of 680 individual lots of medical grade UHMWPE that were produced between 1998 and 2001. The breakdown of the individual lots in the total data set, according to resin and conversion method, is summarized in Table 2.4, and indicates a relatively even distribution between resins and conversion methods.

Not surprisingly, the data reported by the converters for contemporary UHMWPE was found to exceed the requirements for Types 1 and 2 resins, as set forth in ASTM F648. For density, resin but not conversion method was found to be a significant factor (Table 2.5). For the impact strength and the tensile mechanical properties, resin as well as conversion method were both found to be significant factors (Table 2.5). Although statistically significant, differences in the density and tensile properties of UHMWPE were in general not substantial (less than 21% difference in means between the Extruded GUR 1020 and Molded GUR 1050).

Note that this study did not evaluate differences between converters, which could be another source of variation in material properties of UHMWPE. Because the sintering conditions can significantly influence the density, as well

Table 2.5
Summary of Mean (± Standard Deviation) Physical and Tensile Mechanical Properties of Extruded and Molded UHMWPE

Material	Density (kg/m^3)	Tensile yield (MPa)	Ultimate tensile strength (MPa)	Elongation to failure (%)
Extruded GUR 1020	935 ± 1	22.3 ± 0.5	53.7 ± 4.4	452 ± 19
Molded GUR 1020	935 ± 1	21.9 ± 0.7	51.1 ± 7.7	440 ± 32
Extruded GUR 1050	931 ± 1	21.5 ± 0.5	50.7 ± 4.2	395 ± 23
Molded GUR 1050	930 ± 2	21.0 ± 0.7	46.8 ± 6.4	373 ± 29

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as the mechanical properties of UHMWPE, one should not make conclusions of preferred resin and processing method without having all relevant data available from a particular converter.

Studies have reported subtle differences in the morphology and fatigue crack propagation behavior of extruded versus compression-molded UHMWPE. For example, investigations of UHMWPE morphology suggest that compression-molded material has an isotropic crystalline orientation, whereas the morphology in ram extruded UHMWPE varies slightly as a function of the distance from the centerline (Bellare and Cohen 1996). Similarly, crack propagation studies have found more isotropic crack propagation behavior in compression-molded sheets as opposed to ram extruded rods of UHMWPE (Pruitt and Bailey 1998).

Machining: From Consolidated Form to Implant

Orthopedic manufacturers generally machine UHMWPE components into their final form. Even components that are direct molded may be machined on the back surface to accommodate a locking mechanism. However, the actual morphology of machining marks depends on the manufacturing conditions as well as the type of UHMWPE material (e.g., conventional versus highly crosslinked) (Kurtz 2002). An example of machining marks in an as-machined (never implanted) GUR 1050 UHMWPE component is shown in Figure 2.10.

Machining of UHMWPE components consists of milling and turning operations for both roughing and finishing steps. In some cases, the resin converter may supply the stock in a shape that approximates the cross-section of the finished implant. Such preshaping or preforming offers advantages of efficiency and speed to the manufacturer. Because UHMWPE can be damaged

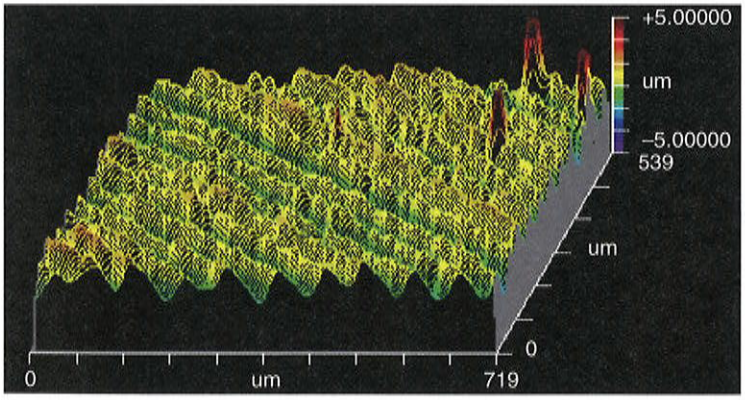


Figure 2.10
An example of machining marks in an as-machined (never implanted) GUR 1050 UHMWPE component.

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by excessive heat, the feed rate, tool cutting force, and spindle speed must be closely monitored during manufacture. Close mechanical tolerances generally require the manufacturing environment temperature to be carefully controlled. Milling machine spindles in the early to mid-1980s could develop up to 4000 rpm, whereas newer machinery can develop up to 8000 rpm; the latest machines develop speeds of 12,000 rpm. Overheating of the UHMWPE is avoided by proper optimization of the feed rate and tool cutting force during machining operations.

The actual cutting speeds, tool feed rates, and depths of cut used to machine UHMWPE components are proprietary, and hence little information is available in the literature about the effect of machining parameters on the tribological properties of UHMWPE (Song et al. 1999). Song and colleagues (1999) have proposed an idealized model for the surface morphology of as-machined UHMWPE as a triangular wave, in which the peak-to-peak distance, d, is given by the following equation:

$$d = \frac{f}{2s}$$

where f is the tool feed rate and s is the cutting speed. Song's model also proposes that the base angle of the machining marks is related to the geometry of the cutting tool. Given the numerous (potentially interrelated) factors influencing the surface topology of as-manufactured components, it is difficult (based on measurements of the surface alone) to quantify the machining conditions used to produce the surface finishes of a randomly sampled component.

Cooper and colleagues (1993) have classified abrasive wear in UHMWPE as involving macroscopic or microscopic asperity contact between the sliding surfaces. Because of the initial difference in surface roughness at the UHMWPE and metal counterfaces, the initial wear rate involves the removal of the larger macroscopic asperities on the UHMWPE surface, whereas the long-term wear rate is governed by the microscopic asperity size of the metal counterface (Cooper, Dowson, and Fisher 1993). Thus, changes to the surface roughness of UHMWPE components may be expected to affect the initial wear rate, because removal of machining marks will occur within the contact zone during the first stages of wear in an orthopedic bearing (Wang, Stark, and Dumbleton 1995).

Conclusion

As will be shown in Chapter 4, the first UHMWPE hip components were produced by Charnley in his home workshop or in the machine shop at Wrightington starting in 1962. The sophistication of the implant manufacturing process has changed considerably since that time. Because of the complexities inherent in producing UHMWPE implants, three highly specialized industries have developed since the 1960s to address different stages of the production pipeline. Polymer resin producers, such as Ticona, focus on polymerization of medical grade UHMWPE resin, whereas a separate industry of converters has

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evolved to address consolidation of UHMWPE into semifinished stock materials, catering to the needs of orthopedic manufacturers. The task of implant design, UHMWPE selection, implant machining, packaging, sterilization, and distribution typically fall within the purview of orthopedic manufacturers.

The choice of conversion method (and converter) is at least as important a decision as the choice of resin for an UHMWPE component, because both factors introduce a subtle change in the morphology and material properties of the consolidated polymer. However, there is currently no consensus as to which resin and conversion method would be universally superior for all orthopedic applications. Consequently, it is left to each orthopedic manufacturer to determine which conversion method (and resin) is most appropriate for applications in hip, knee, shoulder, and spine implants.

References

Baldini T.H., C.M. Rimnac, and T.M. Wright. 1997. The effect of resin type and sterilization method on the static (J-integral) fracture resistance of UHMW polyethylene. *Orthopaedic Research Society* 43:780.

Barnetson A., and P.R. Hornsby. 1995. Observations on the sintering of ultra-high molecular weight polyethylene (UHMWPE) powders. *J Materials Sci Letters* 14:80–84.

Bastiaansen C.W.M., H.E.H. Meyer, and P.J. Lemstra. 1990. Memory effects in polyethylenes: influence of processing and crystallization history. *Polymer* 31: 1435–1440.

Bellare A., and R.E. Cohen. 1996. Morphology of rod stock and compression-moulded sheets of ultra-high-molecular-weight polyethylene used in orthopaedic implants. *Biomaterials* 17:2325–2333.

Biomet. 1995. Resin consolidation issues with UHMWPE. Report No. Y-BEM-069. Warsaw.

Biomet. 1997. ArCom processed polyethylene. Report No. Y-BMT-503. Warsaw.

Birnkraut H.W. 1991. Synthesis of UHMWPE. In *Ultra-high molecular weight polyethylene as a biomaterial in orthopedic surgery.* H.G. Willert, G.H. Buchhorn, and P. Eyerer. Eds. Lewiston, NY: Hogrefe & Huber.

Blunn G.W., A.B. Joshi, R.J. Minns, et al. 1997. Wear in retrieved condylar knee arthroplasties. A comparison of wear in different designs of 280 retrieved condylar knee prostheses. *J Arthroplasty* 12:281–290.

Chen K.C., E.J. Ellis, and A. Crugnola. 1981. Effects of molding cycle on the molecular structure and abrasion resistance of ultra-high molecular weight polyethylene. *ANTEC '81* 39:270–272.

Chubberley A.H. 1965. Ultra-high molecular weight polyethylenes. In *Modern plastics encyclopaedia.* New York: McGraw-Hill.

Cooper J.R., D. Dowson, and J. Fisher. 1993. Macroscopic and microscopic wear mechanisms in ultra-high molecular weight polyethylene. *Wear* 162–164, 378–384.

Edidin A.A., and S.M. Kurtz. 2001. Development and validation of the small punch test for UHMWPE used in total joint replacements. In *Functional biomaterials.* N. Katsube, W. Soboyejo, and M. Sacks. Eds. Winterthur, Switzerland: Trans Tech Publications.

Eyerer P., R. Ellwanger, H.A. Federolf, et al. 1990. Polyethylene. In *Concise encyclopaedia of medical and dental materials.* D. Williams, and R. Cahn. Eds. Oxford: Pergamon.

IPR2024-00493
Honeywell International Inc. v. DSM IP Assets, B.V.
DSM Ex. 2002, Page 40 of 44

Eyerer P., A. Frank, and R. Jin. 1985. Characterization of ultrahigh molecular weight polyethylene (UHMWPE): Extraction and viscometry of UHMWPE. *Plastverarbeiter* 36:46–54.

Farrar D.F., and A.A. Brain. 1997. The microstructure of ultra-high molecular weight polyethylene used in total joint replacements. *Biomaterials* 18:1677–1685.

Goldman M., R. Gronsky, R. Ranganathan, and L. Pruitt. 1996. The effects of gamma radiation sterilization and aging on the structure and morphology of medical grade ultra-high molecular weight polyethylene. *Polymer* 37:2909–2913.

Gsell R., R. King, and D. Swarts. 1997. Quality indicators of high-performance UHMWPE. Warsaw, IN: Zimmer.

Gul R. 1997. Improved UHMWPE for use in total joint replacement. Ph.D. diss., Massachusetts Institute of Technology.

Halldin G.W., and I.L. Kamel. 1977a. Powder processing of ultra-high molecular weight polyethylene. I. Powder characterization and compaction. *Poly Eng Sci* 17:21–26.

Halldin G.W., and I.L. Kamel. 1977b. Powder processing of ultra-high molecular weight polyethylene. II. Sintering. *ANTEC 77* 35:298–300.

Hamilton J.V., H.C. Wang, and C. Sung. 1996. The effect of fusion defects on the mechanical properties of UHMWPE. Trans 5th World Biomater Conference 2:511.

Han K.S., J.F. Wallace, R.W. Truss, and P.H. Geil. 1981. Powder compaction, sintering, and rolling of ultra-high molecular weight polyethylene and its composites. *J Macromol Sci Phys* B19:313–349.

Kurtz S.M., L. Pruitt, C.W. Jewett, et al. 1998. The yielding, plastic flow, and fracture behavior of ultra-high molecular weight polyethylene used in total joint replacements. *Biomaterials* 19:1989–2003.

Kurtz S.M., O.K. Muratoglu, M. Evans, and A.A. Edidin. 1999. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. *Biomaterials* 20:1659–1688.

Kurtz S.M., J. Turner, M. Herr, and A.A. Edidin. 2002. Deconvolution of surface topology for quantification of initial wear in highly crosslinked acetabular components for THA. *JBMR (Applied Biomaterials)* 63:492–500.

Kusy R.P., and J.Q. Whitley. 1986. Use of a sequential extraction technique to determine the MWD of bulk UHMWPE. *J Appl Poly Sci* 32:4263–4269.

Li S., and A.H. Burstein. 1994. Ultra-high molecular weight polyethylene. The material and its use in total joint implants. *J Bone Joint Surg Am* 76:1080–1090.

Lykins M.D., and M.A. Evans. 1995. A comparison of extruded and molded UHMWPE. *Trans 21st Soc Biomater* 18:385.

McKenna G.B., J.M. Crissman, and F. Khoury. 1981. Deformation and failure of ultra-high molecular weight polyethylene. *ANTEC '81* 39:82–84.

Muratoglu O.K., M. Jasty, and W.H. Harris. 1997. High resolution synchrotron infra-red microscopy of the structure of fusion defects in UHMWPE. Transactions of the 43rd Orthopedic Research Society 22:773.

Olley R.H., I.L. Hosier, D.C. Bassett, and N.G. Smith. 1999. On morphology of consolidated UHMWPE resin in hip cups. *Biomaterials* 20:2037–2046.

Pruitt L., and L. Bailey. 1998. Factors affecting the near-threshold fatigue behavior of surgical grade ultra high molecular weight polyethylene. *Polymer* 39:1545–1553.

Schmidt M.B., and J.V. Hamilton. 1996. The effects of calcium stearate on the properties of UHMWPE. 42nd Orthopedic Research Society 21:22.

Shenoy A.V., and D.R. Saini. 1985. Compression moulding of ultra-high molecular weight polyethylene. *Plast Rubber Proc Appl* 5:313–317.

IPR2024-00493
Honeywell International Inc. v. DSM IP Assets, B.V.
DSM Ex. 2002, Page 41 of 44

Song J., P. Liu, M. Cremens, and P. Bonutti. 1999. Effects of machining on tribological behavior of ultra-high molecular weight polyethylene (UHMWPE) under dry reciprocating sliding. *Wear* 225–229:716–723.

Stein H. Personal communication. 8 July 1997.

Swarts D., R. Gsell, R. King, et al. 1996. Aging of calcium stearate-free polyethylene. Trans 5th World Biomater Conference 2:196.

Truss R.W., K.S. Han, J.F. Wallace, and P.H. Geil. 1980. Cold compaction molding and sintering of ultra-high molecular weight polyethylene. *Poly Engr Sci* 20:747–755.

Voigt-Martin I.G., E.W. Fisher, and L. Mandelkern. 1980. Morphology of melt-crystallized linear polyethylene fractions and its dependence on molecular weight and crystallization temperature. *J Poly Sci (Poly Phys)* 18:2347–2367.

Wagner H.L., and J.G. Dillon. 1988. Viscosity and molecular weight distribution of ultra-high molecular weight polyethylene. *J Appl Poly Sci* 36:567–582.

Walker P.S., G.W. Blunn, and P.A. Lilley. 1996. Wear testing of materials and surfaces for total knee replacement. *J Biomed Mater Res* 33:159–175.

Wang A., C. Stark, and J.H. Dumbleton. 1995. Role of cyclic plastic deformation in the wear of UHMWPE acetabular cups. *J Biomed Mater Res* 29:619–626.

Wang X.Y., S.Y. Li, and R. Salovey. 1988. Processing of ultra-high molecular weight polyethylene. *J Appl Poly Sci* 35:2165–2171.

Weightman B., and D. Light. 1985. A comparison of RCH 1000 and Hi-Fax 1900 ultra-high molecular weight polyethylenes. *Biomaterials* 6:177–183.

Wrona M., M.B. Mayor, J.P. Collier, and R.E. Jensen. 1994. The correlation between fusion defects and damage in tibial polyethylene bearings. *Clin Orthop* 299:92–103.

Zachariades A.E. 1985. The effect of powder particle fusion on the mechanical properties of ultra-high molecular weight polyethylene. *Poly Engr Sci* 25:747–750.

Chapter 2. Reading Comprehension Questions

2.1. When was UHMWPE first commercially introduced for industrial applications?
a) 1940s
b) 1950s
c) 1960s
d) 1970s
e) 1980s

2.2. What trace impurities are present in UHMWPE after polymerization?
a) Chlorine
b) Aluminum
c) Titanium
d) Ash
e) All of the above

2.3. Which of the following is a trade name for UHMWPE resin that contains calcium stearate?
a) RCH 1000
b) GUR 1050
c) GUR 415
d) Chirulen
e) All of the above

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2.4. For which of the following reasons would calcium stearate be added to UHWMPE?
a) Scavenge residual catalyst
b) Decrease specific gravity
c) Improve impact strength
d) Reduce consolidation time
e) All of the above

2.5. Which of the following UHMWPE resins has the highest molecular weight?
a) GUR 1020
b) GUR 1050
c) Teflon
d) Chirulen
e) RCH 1000

2.6. The molecular weight of UHMWPE is most commonly inferred from which material property?
a) Impact strength
b) Tensile strength
c) Density
d) Intrinsic viscosity
e) Small punch test

2.7. Which of the following conversion techniques CANNOT be used to process UHMWPE resin powder?
a) Isostatic molding
b) Net shape molding
c) Compression molding
d) Injection molding
e) Ram extrusion

2.8. Which of the following factors influence the machining of UHMWPE implants?
a) Tool feed rate
b) Tool cutting force
c) Heat generation
d) Spindle speed
e) All of the above

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Biomedical Engineering

The UHMWPE Handbook

Ultra-High Molecular Weight Polyethylene in Total Joint Replacement

Each year, over 1 million patients around the world are implanted with artificial hip and knee joints. Ultra-high molecular weight polyethylene (UHMWPE) is used as the bearing material in the vast majority of these total joint replacements. Although the use of UHMWPE has proven to be very successful over the past four decades, the longevity of joint reconstructions may be limited to around 10 years. Continuous enhancement of UHMWPE biomaterials is necessary to improve the long-term performance of joint replacements.

The 15 chapters of *The UHMWPE Handbook* describe the history, properties, and clinical performance of biomaterials used for joint replacement, and provides the key to understanding the world literature of UHMWPE and joint replacement. The historical and contemporary references to implant biomaterials for the hip and knee are reviewed in detail. The clinical application of UHMWPE is covered comprehensively. Not only are hip and knee replacement performance reviewed, but also emerging fields of joint replacement, including shoulder and disc replacement surgery, are discussed in dedicated chapters.

State-of-the-art alternative bearing technologies for joint replacements are reviewed. Chapters are devoted to ceramic-on-ceramic, metal-on-metal, and highly crosslinked UHMWPE materials in hip and knee replacement.

Each chapter concludes with reading comprehension questions, to aid in undergraduate or graduate instruction.

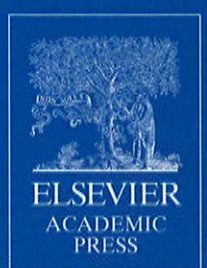
The UHMWPE Handbook is the comprehensive reference for students, researchers, and surgeons interested in biomaterials technologies for total joint replacement surgery.

Steven M. Kurtz is the leading international authority on UHMWPE materials and their engagement. Dr. Kurtz received his Ph.D. from Drexel University, where he studied the role of oxidative degradation on the contact mechanics of hip and knee replacements. He has authored dozens of peer-reviewed articles about UHMWPE materials, and written both national and international standards for UHMWPE materials used in joint replacement. Dr. Kurtz is a Principal Engineer at Exponent, Inc., where he consults with orthopedic implant producers on new technologies for joint replacement surgery. He is the Director of Exponent's Philadelphia office. Dr. Kurtz also directs a hip and knee implant retrieval program at Drexel University to determine how UHMWPE materials change after implantation in the human body.

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