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TECHNISCHE UNIVERSITÄT WIEN Vienna University of Technology

Dissertation

Structure-properties correlations in PE-UHMW: influence of consolidation, crosslinking, sterilization, and *in vivo* use on hip implants

ausgeführt zum Zwecke der Erlangung des akademischen Grades einer Doktorin der technischen Wissenschaften

unter der Leitung von

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Abstract

The most important medical application of ultra high molecular weight polyethylene (PE-UHMW) is the replacement of damaged cartilages in total joint replacement surgery. The PE-UHMW component is the limiting part of the artificial joint mainly due to wear and oxidative degradation. In many cases, the precise mechanisms responsible for the failure of the components remain unclear. Not only manufacturing and irradiation (with the purpose of sterilization or cross-linking of PE-UHMW) but also thermal treatment and *in vivo* use, significantly alter the chemical architecture of the polymer and the resulting microstructure. These modifications result in changes of the mechanical properties of the material.

The aim of this thesis is to correlate structural parameters at molecular level and at nanometer scale to the micro- and macro-mechanical behavior of PE-UHMW used for hip joint implants. It is investigated how the structure and properties of the material are influenced by PE-UHMW resin type, additivation by vitamin E, the manufacturing techniques (ram extrusion or compression molding), irradiation procedure, post-irradiation thermal treatment, and *in vivo* use. The resulting anisotropy is investigated on a micrometer scale.

Fourier Transform Infra Red Spectroscopy (FTIR) and differential scanning calorimetry (DSC) assess the chemical structure and the molecular organization in the material comprehensively. The influences of oxidative degradation and total irradiation dose on morphology are evaluated. DSC experiments enable calculation of average thickness of crystalline and amorphous phase, lamellar thickness distribution, and the probability of formation of tie molecules. The results are related to mechanical properties at micrometer level investigated by Depth Sensing Indentation technique (DSI). A new test method, based on the fracture mechanical J-integral concept, is presented. This method allows investigation of the fracture behavior of PE-UHMW on component level.

The consolidation process leads to thermo-oxidative degradation of the surface layers, especially during ram extrusion. Gamma-sterilized and crosslinked PE-UHMW implants stabilized by annealing show enhance susceptibility to oxidation. Consolidated material, manufactured and crosslinked hip implants stabilized by remelting show less tendency to oxidize.

The morphology is influenced by molar mass: higher molar mass results in a lower degree of crystallinity. Oxidative degradation and chain scission due to irradiation result in recrystallization of the liberated polymer chain segments. Gamma-irradiation leads to an increase in crystallinity due to refinement of existing lamellae and the generation of a second population of small lamellae. Crosslinking and remelting reduce the degree of crystallinity. The crosslinks formed during remelting hinder crystallization. The corresponding lamella thickness distribution depends on the temperature during irradiation: irradiation at 120 °C leads to a bimodal lamellar thickness distribution, whereas irradiation at 40 °C results in a very broad lamellar thickness distribution. Crosslinking and annealing leads to an elevated degree of crystallinity and a high amount of thick lamellae in the material. The probability of occurrence of tie molecules (calculated from DSC data) is similar in the PE-UHMW material states. Comparison with literature data shows that the probability of occurrence of tie molecules reaches a plateau above 1×10^6 g/mol.

An increase in degree of crystallinity leads to higher micro-hardness and indentation modulus. The small lamellae in gamma-sterilized PE-UHMW adversely affect the micromechanical properties. Biomolecules diffused into a hip implant during *in vivo* use evoke a plasticizer effect; this reduces the hardness and the indentation modulus in areas where these molecules are analyzed.

Consolidation method, molar mass, and additivation by vitamin E do not influence the J determined fracture toughness. Gamma-irradiation reduces the fracture toughness of hip implants. Crosslinking further reduces the toughness and changes the fracture behavior the resistance against stable crack growth is further reduced. Remelting leads to a bigger reduction

than annealing does. The temperature at irradiation has no influence. The fracture process in PE-UHMW does not involve cavitations in front of the crack tip. The mobility of the amorphous phase in terms of concentration of terminal vinyl group influences the fracture behavior. The technical crack initiation decreases with decreasing concentration of the terminal vinyl group together with decreasing thickness of amorphous phase.

Production processes induce anisotropy only in the consolidation step. Structural and mechanical anisotropy is essentially developing during *in vivo* use. Nevertheless, it is founded in the manufacturing processes, e.g. gamma-sterilization or crosslinking procedure.

Kurzfassung

Hüftpfannen aus ultra hochmolekularem Polyethylen (PE-UHMW) sind seit den 1960er Jahren als Gleitflächenersatz in der Hüftgelenks- Endoprothetik im Einsatz. Die häufigste Versagensursache dieses Gelenksersatzes ist derzeit Implantatlockerung aufgrund von Abriebpartikeln aus PE-UHMW, da diese im menschlichen Körper zu Knochenabbaureaktionen führen können. Um das Verschleißverhalten *in vivo* zu verbessern sind zurzeit überwiegend vernetzte PE-UHMW Hüftpfanneneinsätze am Markt. Die Vernetzung erfolgt durch gamma- oder Elektronen-Bestrahlung des konsolidierten Werkstoffes. Um die danach im Polymer vorhandene Makroradikalkonzentration zu senken, folgt eine thermische Nachbehandlung (Schmelzen oder Tempern). Nach Fertigung des Implantats wird dieses abschließend Strahlen- oder Gassterilisiert.

Ziel dieser Arbeit ist es die Struktur des Werkstoffes während des Lebenszyklus der Hüfpfanneneinsätze auf molekularer und Nanometer-Ebene zu charakterisieren und zu den mikro- und makro- mechanischen Eigenschaften zu korrelieren. Es wird beschrieben wie Molmasse, Additivierung mit Vitamin E, Konsolidierungsverfahren (Strangpressen oder Presssintern), Bestrahlung (mit dem Ziel Sterilisation oder Vernetzung), thermischer Nachbehandlung und *in vivo* Gebrauch Morphologie und Eigenschaften beeinflussen. Durch Herstellung und Gebrauch induzierte Anisotropie wird auf Mikrometer-Ebene untersucht.

Die chemische Architektur des Polymers und die daraus resultierende Morphologie des Werkstoffes werden mit Fourier transformierter Infrarotspektroskopie (FTIR) und dynamischer Differenz- Thermoanalyse (DSC) untersucht: Die Morphologie wird von der Molmasse beeinflusst. Geringere Molmasse resultiert in einem höheren Kristallinitätsgrad. Kettenabbau durch oxidative Degradation oder Bestrahlung führt zu Rekristallisation der freigesetzten Molekülsegmente. Gamma-Bestrahlung führt zu einer Erhöhung des Kristallinitätsgrades durch Vergrößerung bereits vorhandener Kristallite und zur Entstehung einer zweiten Kristallit- Population mit geringer Lamellendicke. Strahlen-Vernetzung und anschließendes Schmelzen des Werkstoffes führen zu einer Reduktion des Kristallinitätsgrades: die entstandenen Vernetzungspunkte im Polymer verändern das Kiristallisationsverhalten und behindern die Kristallisation. Die resultierende Lamellendickenverteilung hängt von der Temperatur während der Bestrahlung ab. Bestrahlung bei 120 °C (kleine Lamellen bereits geschmolzen) führt zur eine bimodalen Lamellendickenverteilung während Bestrahlung bei 40 °C zu einer sehr bereiten Lamellendickenverteilung führt. In beiden Fällen ist diese durch die Vernetzungspunkte fixiert. Strahlen-Vernetzung und anschließendes Tempern führt zu einer Erhöhung des Kristallinitätsgrad. Die Lamellendickenverteilung im Werkstoff weist eine große Menge dicker Lamellen (33 – 70 nm) auf und ist nicht durch die Vernetzungspunkte fixiert da die Effekte des Temperns reversibel sind.

Die Wahrscheinlichkeit zur Bildung von Tie Molekülen (berechnet aus DSC Daten) ist für die untersuchten Werkstoffzustände sehr ähnlich. Durch Vergleich mit Literaturdaten zeigt sich, dass die Wahrscheinlichkeit zur Bildung von Tie Molekülen bei einer Molmasse von $> 1 \times 10^6$ g/mol ein Plateau erreichen.

Die mikro-mechanischen Eigenschaften der Werkstoffzustände wurden mittels instrumentierter Eindringprüfung (DSI) ortsaufgelöst untersucht. Eine erhöhter Kristallinitätsgrad führt zu erhöhter Mikrohärte und erhöhtem Eindringmodul. Die während der gamma- Sterilisation generierten kleinen Lamellen wirken sich negativ auf die mikro-mechanischen Eigenschaften aus. Während des *in vivo* Gebrauchs diffundieren Biomoleküle aus der, das Implantat umgebenden Synovialflüssigkeit, in das Polymer ein. Diese Biomoleküle bewirken in höherer Konzentration eine Weichmachung des Werkstoffes: In jenen Implantatbereichen, wo die Härte und der Eindringmoduls herabgesetzt sind, können sie nachgewiesen werden.

Zurzeit ist in der Literatur keine Methode beschrieben, die es ermöglicht Hüftpfanneneinsätze direkt mit bruchmechanischen Methoden zu charakterisieren. Daher wurde eine Prüfmethode auf der Basis des J-Integral Konzeptes entwickelt, die es erlaubt die Wechselwirkung eines

Risses mit dem Werkstoff durch Risswiderstandskurven (J-R Kurven) zu beschreiben. Somit sind die Auswirkungen des Herstellungsprozesses auf die Zähigkeit des Bauteils direkt messbar.

Molmasse, Additivierung mit Vitamin E and Konsolidierungsverfahren zeigen keinen Einfluss auf die Rissinitiierung und das energiedeterminiert Bruchverhalten. Gamma-Sterilisation setzt die Zähigkeit des Werkstoffes herab. Vernetzung führt zu noch geringerer Zähigkeit und bewirkt eine Veränderung des Bruchverhaltens. Die J-R- Kurven zeigen einen geringeren Widerstand gegenüber stabiler Rissausbreitung auf. Schmelzen nach Bestrahlung setzt die Zähigkeit mehr herab als Tempern. Die Temperatur während der Bestrahlung hat keinen Einfluss auf Zähigkeit und Bruchverhalten. Ein Riss in PE-UHMW wächst ohne messbare Hohlraumbildung vor der Rissspitze. Verfügbarkeit und Beschaffenheit der amorphen Phase beeinflussen das Bruchverhalten: Der Widerstand gegen Rissinitiierung steigt mit sinkender Temperatur zu Beginn der Kristallisation T_{c,onset} im DSC Experiment (ein Maß für höhere Mobilität der amorphen Phase bei Raumtemperatur). Ein höherer Widerstand gegen Rissinitiierung korreliert mit einer höheren Konzentration an terminale Doppelbindungen (Maß für geringere Y-Vernetzung bzw. höhere Temperatur während der Konsolidierung) zusammen mit einer größeren durchschnittlichen Dicke der amorphen Phase im Werkstoff.

Messbare Anisotropie wird bei Herstellungsprozess nur im Zuge des Strangpressens in den Werkstoff eingebracht. Strukturelle und mechanische Anisotropie entsteht vorwiegen während des *in vivo* Gebrauchs. Sie gründet aber in Herstellungsschritten wie zum Beispiel gamma-Sterilisation oder Strahlenvernetzung mit anschließendem Tempern.

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1 Introduction

Ultra high molecular weight polyethylene (PE-UHMW) is a polyethylene type with molar mass in the range of $3 - 8 \times 10^6$ g/mol [1]. Due to its molar mass PE-UHMW has the highest abrasion resistance and impact toughness compared to polyethylene types with lower molar mass and all other polymers [2]. Furthermore, PE-UHMW bulk material is biocompatible, chemical inert, and has other favorable properties like polyethylene in general. The disadvantage of the high molar mass is the very high melt viscosity impeding melt processing of the polymer, i.e. extrusion, injection molding or blow molding is not practicable. Instead the polymer has to be consolidated by ram extrusion or compression molding. PE-UHMW is used in chemical engineering, food -, electronics – and textile industry, mining and transportation. Especially machine parts subjected to wear are made from PE-UHMW, e.g. bearings, gears, linings, and chain guides [3]. Around 2 % of the annual world production is used in biomedical applications [4].

The choice of PE-UHMW as a bearing material in total joint replacement originates from its superior biomechanical properties – low friction coefficient, high toughness, good biocompatibility and enhanced resistance to creep [5]. Sir John Charnley introduced PE-UHMW articulating against a metallic femoral head first in 1962 and it has been very successfully in this application since then. Nevertheless, the PE-UHMW component limits the lifetime of the implant. This limitation arises because of the generation of mechanically induced polymer wear debris at the articulating surface [6-9]. These wear particles cause tissue reactions leading to resorption of bone, culminating in loosening and hence the failure of the prosthesis [10].

Different PE-UHMW types (in terms of molar mass and mechanical) are used in orthopedic applications. According to standard regulations no stabilizers or processing aids may be added to the medical grade PE-UHMW during manufacturing. Hence the material is not protected against degradation by the means of additives. An efficient stabilizer against oxidative degradation in the human body is vitamin E [11]. Recently PE-UHMW stabilized by vitamin E has been approved by the food and drug administration for the use in hip implants.

In order to reduce *in vivo* wear, radiation crosslinked and thermally stabilized [5,10] PE-UHMW has been clinically introduced in the late 1990's [12]. These procedures enhance wear behavior [13] but reduces other mechanical properties including strength, ductility, fracture toughness, and crack propagation resistance [14-19]. However, these properties are important to the long-term success of PE-UHMW components used in total joint replacements [14, 20]. Therefore, a second generation highly crosslinked PE-UHMW has been developed by stabilizing the polymer with different methods e.g. additivation by vitamin E, sequential irradiation and thermal treatment ... [20], in order to optimize the properties. The clinical success of these material modifications has to be closely monitored over years from now [13].

After manufacturing, cleaning, packaging and labeling the implants have to be sterilized. Today irradiation sterilization under inert atmosphere in gas impermeable packaging is favored, since the adverse effects of oxidation induced PE-UHMW embrittlement related with irradiation-sterilization in oxygen containing atmosphere have been reported [21-23]. Gas sterilization methods (using gas plasma or ethylene oxide) are successfully employed too. Both methods do not modify the mechanical behavior of PE-UHMW substantially [24-27].

Manufacturing, irradiation, thermal treatment and *in vivo* use significantly alter the microstructure of PE-UHMW hip endoprosthesis during its life cycle. Especially properties like the fracture toughness of a semicrystalline polymer are highly affected by changes in the microstructure. Furthermore, the relations between material properties, wear and clinical performance are not understood yet.

The aim of this Thesis is to establish structure-properties correlations. The interdependencies of chemical and physical structure and micro- and macro-mechanical properties are related to the demands on PE-UHMW hip components during their life cycle. Furthermore, structural and mechanical anisotropy induced during the life cycle is investigated.

Extend and mechanism of oxidative degradation, effects of irradiation on the chemical structure and concentration of biomolecules diffused into the polymer during *in vivo* use are investigated by Fourier transformed infrared spectroscopy (FTIR). The morphology is characterized by the degree of crystallinity, average thickness of crystalline and amorphous phase, lamellar thickness distribution, probability of tie molecule formation and tie molecule area fraction at crystalline-amorphous interface. These characteristic values are calculated from differential scanning calorimetry (DSC) measurements.

Micromechanical properties are determined by means of depth sensing indentation technique (DSI). This quasi-nondestructive testing method requires very small sample volumes. Hence, investigations related to a specific location within the implant are possible.

These methods are used to investigate anisotropy. "Mapping" of characteristic values e.g. from surface inwards and in different regions of hip implants, is enabled.

The fracture behavior of PE-UHMW is very important for the longevity of hip implants. A method for testing PE-UHMW hip components on the basis of the fracture mechanical J-integral concept is presented in this Thesis. This new tool enables direct evaluation of the fracture behavior of implants as available for surgeons and patients. Consolidated new material modification (PE-UHMW containing vitamin E) and hip implants are compared in terms of resistance against crack growth (J-R curves) and technical crack initiation. The fracture mechanism is evaluated by fractography.

The investigations concern chemical structure, morphology, micro-mechanical properties, and fracture toughness of consolidated material (ram extruded and compression molded, with and without vitamin E), manufactured, gamma-sterilized, and commercially available crosslinked (first and second generation) PE-UHMW hip implants. The results are exemplarily related to the structure and properties of implants after *in vivo* use (originally made from similar material states).

2 Ultra high molecular weight polyethylene (PE-UHMW) in orthopedic application

2.1 The use of PE-UHMW in total hip replacement

At the present, the most important biomedical application of PE-UHMW is the replacement of damaged cartilages in total joint replacement surgery. Total joint replacement of hip and knee is one of the most common orthopedic surgeries today. The demand of these surgeries is growing rapidly due to higher life expectancy (EU, USA), sporting accidents of younger patients and increase in revision surgeries. Till 2030, a huge increase in total hip joint replacement and total knee replacement is expected (see Figure 1) [5].



Figure 1: Projected growth of primary total hip (THA) and knee (TKA) procedures in the USA till 2030 [5]

Additionally, the requirement for the service time of endoprosthetic components increases due to aging of the population. At the moment total joint replacement is revised at a rate of 1 % or lower during the first ten years *in vivo*. The survivorship decreases markedly after 10 years [28]. An increase in average survivorship of the implant will help the patients, lower social and economic costs, and create the possibility of implantation in younger, more active patients [6]. The success of a joint replacement implant is related with many interdepending factors. Some factors concern the design and production of the implant systems, some are surgeon-related (e.g. implantation technique) and some are patient-related (e.g. biological reactions on wear particles, body weight, activity, general medical status) [29].

Generally, implant development tends to replace foreign material to the body by body's own or similar material. This process starts at the moment and the success depends on the function of the implant under investigation. In the case of load bearing joint implants, there will be a huge demand of research to get the final clinical products and new strategies including "Biosurface Engineering" have to be developed [30].

Clinically the focus lies on expanding the lifetime of the natural joint. For example, cartilage resurfacing techniques are used and research on hydrogels for cartilage replacement is intensified. The potential of other polymeric materials (e.g. polycarbonate-urethane elastomer PCU) for use in orthopedic application is evaluated currently [31]

There are three material classes in clinical use at the moment:

- Polymer ultra-high molecular weight polyethylene (PE-UHMW) and acrylic resin cements in cemented endoprothsesis systems
- Metal mainly stainless steel, titanium, and cobalt-chromium based alloys
- Ceramic mainly aluminia and zirconia

The EN 12010:1998 [29] relates to further specifications of the materials which are approved or inapplicable for use in joint replacement implants.

Figure 2 shows the general design of a hip endoprosthesis and position *in vivo*. The total joint endoprosthesis systems are designed to fully substitute the function (and feeling) of the natural hip joint.



Figure 2: Components of a hip endoprosthesis: hard – soft combination (left) [32]; hard-hard (ceramic-ceramic) combination (middle) [33]; X-Ray image of a total hip joint replacement (right) [34]

The materials are employed in order to get two different tribological couplings:

- hard soft: the femoral head is made from metal or ceramic and the acetabular liner is made from PE-UHMW (Figure 2, left). In these systems boundary lubrication dominates. It is the most "forgiving" coupling with respect to male-positioning.
- hard hard: both, the femoral head and the acetabular liner are made from metal (metal on metal combination), ceramic (ceramic on ceramic combination, Figure 2, middle), or ceramic and metal (ceramic on metal);

There are also acetabular liners made from PE-UHMW in clinical use where the articulating surface is covered by metal or ceramic. This design should combine the damping properties of the polymer with the hard, abrasion resistant properties of metals or ceramics.

A very important factor for the long term success of the prosthesis is tribological behavior *in vivo* and the generation of mechanically induced wear particles. Understanding the history of wear in a clinical setting is the first step in improving longevity in total hip replacement [28]. PE-UHMW wear particles can cause adverse tissue reactions. PE-UHMW particles are bioinert but biological active: The body cells try to phagocytose them, but it is not possible. Hence, biochemical reactions are triggered which lead to resorption of bone, culminate in loosening and revision surgery [10,35,36]. This PE-UHMW "particle disease" is called aseptic loosening or osteolysis and it is one of the most common reason for revision surgery, especially if the revision surgery is many years after primary operation [37]. In Figure 3 data concerning the reasons of revision surgery from the Swedish Hip Arthoplasty Register [37] are shown (no register is available in Austria; the European Union tries to establish an EU-wide register currently).



Figure 3: Distribution of reason to revision 1999 and 2003 –2008 (left) and distribution of reason to first-time revision related to time of primary total hip replacement (right); both diagrams from [37]

Nevertheless, deep infection [37] and dislocation [28] are more frequently reported reason for revision surgery in the last years. Partly, this may be attributed to the fact that in the 1990s crosslinked PE-UHMW was clinically introduced as one approach to reducing wear and increase longevity of total hip prosthesis [13]. The wear properties of crosslinked PE-UHMW acetabular liners are superior to conventional, non-crosslinked PE-UHMW *in vitro* [38-42] and *in vivo* [13,43]. Figure 4 shows exemplarily the wear behavior *in vitro* of crosslinked and non-crosslinked PE-UHMW.



Figure 4: In vitro (hip simulator) wear behavior of PE-UHMW liners [39]: comparison of crosslinked and non-crosslinked PE-UHMW

The crosslinking procedures enhance wear behavior but reduce other mechanical properties of PE-UHMW including strength, ductility, fracture toughness, and crack propagation resistance [15-19]. Furthermore, there are rim fractures of crosslinked PE-UHMW liners *in vivo* reported [44,45] Furmanski et al. [44] attributed the failure of the implants to male-positioning leading to impingement on the posterior rim, and to inadequate prosthesis design employing crosslinked PE-UHMW. The design of endoprosthesis systems was not adapted to the reduced resistance against crack growth in crosslinked PE-UHMW. Design features (e.g. notches)

necessary for locking mechanisms of the liners in the acetabular shell lead to stress concentrations high enough to promote stable crack growth.

Wear is progressive material loss form solid surfaces in contact which occurs as a result of friction. Friction and wear are not material properties but properties of the system in which they operate. There are six fundamental mechanisms of wear: abrasive wear, adhesive wear, fatigue or delamination wear, fretting wear, erosive wear and tribochemical wear [46]. In PE-UHMW hip endoprosthesis abrasive and adhesive wear mechanisms dominate and in knee endoprosthesis fatigue wear is observed additionally [48].

The combination ceramic-ceramic generates the lowest amount of wear (ceramic particles), followed by the metal-metal combination (metal particles and ions) [47]. In the hard - hard systems hydrodynamic lubrication (thickness of fluid film is high enough to completely separate the articulating surfaces) dominates. Hence, the amount of wear generated in the hip endoprosthesis is lower.

The combination PE-UHMW- ceramic generates more PE-UHMW wear and the combination of PE-UHMW-metal generates the highest amount of PE-UHMW wear [47,48]. In hard - soft systems boundary lubrication dominates.

A comparison of wear amount generated *in vivo* and *in vitro* by different articulating materials is shown in Figure 5.



Figure 5: Hip endoprosthesis – *in vivo* linear head penetration (μ m/year), left, and *in vitro* wear rate (mm³/10⁶ cycles), right of different trobological systems [48]

Additionally, Figure 5 shows that *in vivo* wear rates and wear rates determined by tests in hip simulators cannot be compared directly. Hip simulator testes evaluate the tribological behavior to protect the patients (there are different simulators and different testing protocols can be run) [35]. They approximate joint articulation by regard parameters like e.g. applied loads during walking, sliding velocity, lubrication, temperature, and surface texture. Hence, the tribological behavior *in vivo* is estimated, but not fully reflected. The wear rate can be determined by either linear by radiographic (*in vivo*) and shadowgraphic (*in vitro*) wear measurements or volumetric by gravimetry (*in vitro*, most frequently used) [48]. But not only the amount of wear particles but also their number, size, size distribution, and biological activity influence the success of total hip replacement.

Green et al. [49,50] showed that PE-UHMW wear particles in the $0.1 - 1.0 \ \mu m$ size range are the most biologically active, in terms of production of osteolytic cytocines and bone resorption. In non-crosslinked PE-UHMW GUR 1020 (lower molar mass type, see 2.2.2) produces larger wear particles than GUR 1050 (higher molar mass type, see 2.2.2) in hip simulator tests. Hence, the osteolytic potential (functional biological activity FBA) of the non-crosslinked GUR 1020 material is three-fold lower than that of GUR 1050 [51]. In crosslinked material proportional more particles sized between $0.1 - 1.0 \ \mu m$ are generated. Due to dramatic reduction in total wear volume the osteolytic potential of highly crosslinked GUR 1050 is reduced by the approximately 5-fold [51]. Furthermore, it is assumed that there is a threshold value in wear rate of 0.1 mm/year. Above this wear level osteolysis becomes more frequently and extensive [13].

Ceramics are brittle. Fractures *in vivo* lead to catastrophic failures and the success of the revised prosthesis is limited due to third body wear than. Ceramic wear particles in the same size as PE-UHMW particles are generated *in vivo*. But they are less biologically active than PE-UHMW wear particles, and as wear volumes produced in ceramic-on-ceramic prostheses can be up to 4000-fold lower, the volume of ceramic particles *in vivo* may not reach sufficiently high enough levels to elicit an inflammatory response [47].

Metal bearings can cause hypersensitivity and include biological risks associated with elevated metal ion exposure [28]. If sufficient volume of metal particles (nanometer sized) is generated and accumulated in the periprosthetic tissues, it can cause necrosis of the tissues [52].

In the natural joint as well as in the total joint replacement, the articulating surfaces are lubricated by the synovial fluid. The body fluid is a very effective lubricant. It is ultra-filtrated blood plasma, containing water (97 - 99 %), proteins (mainly albumin), electrolytes, and various organic compounds (like hyaluronic acid, non-protein N, phospholipid, cholesterol and uric acid) [53]. As in any body fluid, oxygen is dissolved in the synovial fluid too.

As tribology is a property of the system, not only the materials themselves but also design and patient related factors influence the generation of wear particles. For hard – soft combinations smaller acetabular components and smaller femoral heads lead to favorable lubrication conditions. Less wear is generated when compared with bigger acetabular components and femoral heads. For hard – hard combinations the situation is the other way round. Bigger acetabular components and femoral heads (reduced liner thickness respectively) lead to favorable lubrication conditions and less wear. The relations between wear and physiological function are illustrated in Figure 6.



Figure 6: Physiological function of total hip endoprosthesis related with survivorship in terms of wear (goal: low wear and optimized function) [54]

For the patients, the range of motion is bigger and the risk of dislocation is smaller if bigger acetabular components (liner diameter ≥ 36 mm) and femoral heads are used [55]. The use of big acetabular components and femoral heads is limited by anatomic restrictions, especially in smaller people (e.g. women). These considerations explain the current trend for reducing liner thickness and hence, size of the acetabular component, even in designs employing crosslinked PE-UHMW (with reduced resistance to crack growth). Finally, the surgeon decides which patient gets which prosthesis. The decision is guided by safety, experience and local traditions. PE-UHMW is highly successful used in total hip and knee replacement. Considering the high amount of primary and revision surgeries today and the future demand on these surgeries, the need to prolong the lifetime of the endoprosthesis is obvious. Investigations on structure-properties correlations enable optimization of the polymer properties for this application.

2.2 Manufacturing of PE-UHMW hip liners

Ultra high molecular weight polyethylene is a linear homopolymer produced by polymerization of ethylene gas. Structurally, PE-UHMW is similar to PE-HD differing primarily in the average molecular chain length (PE-HD mostly $< 3 \times 10^5$ g/mol, PE-UHMW $> 3 \times 10^6$ g/mol) [2]. PE-UHMW exhibits the best sliding wear resistance and impact toughness of any polymer resulting from the extremely long polymer chains and the semi-crystalline solid state [2]. An overview about the properties of different polyethylene types is given in Table 1.

	PE-LD	PE-HD	PE-UHMW
degree of crystallinity (%)	40 - 55	60 - 75	50 - 60
density (g/cm3)	0.910 - 0.930	0.945 - 0.965	0.927 - 0.944
melting point (°C)	105 - 115	128 - 137	125 - 145
tensile yield strength (MPa)	6 - 11	15 - 35	19 - 23
elastic modulus (MPa)	100 - 500	400 - 1500	800 - 1600
ultimate tensile strength (MPa)	7 - 16	18 - 40	> 27
elongation at break (%)	50 - 800	40 - 1000	> 300
Shore hardness D		60 - 70	70
double notched impact strength (kJ/m) [2]		0.427	1.495

Table 1: Comparison of structural parameters and	I mechanical properties	of PE-UHMW,	PE-HD and
PE-LD [3]			

The special demands on safety and effectiveness in total joint replacement are reflected in the manufacturing process. The life cycle of a hip implant involves synthesis of the polymer powder, consolidation (via ram extrusion or compression molding), milling and turning of the pre-form and the implant, irradiation crosslinking and thermal treatment, sterilization and *in vivo* use. The individual steps, summarized in Figure 7, will be discussed in this chapter.



Figure 7: Workflow chart of manufacturing process for PE-UHMW hip implants

2.2.1 Synthesis of PE-UHMW

PE-UHMW is synthesized using catalysts based on Ziegler-Natta catalysts- titanium chloride and aluminum alkyls, in liquid slurry [2]. New, more active catalyst systems for PE-UHMW used in implants are developed continuously [28]. The general mechanism is the same as in Ziegler-Natta polymerization. The method is similar to the synthesis of HD-PE except PE-UHMW chains are polymerized to greater lengths. Molecular hydrogen is used as transfer agent to control molecular weight. The resultant polymer chains are remarkably linear. Nevertheless, catalyst chemistry influences average molar mass and distribution, degree of crystallinity, particle size and morphology. In situ modification of PE-UHMW is possible but not practiced [2]. Currently DSM (The Netherlands, Europe) develops a new easy crosslinking PE-UHMW – Easy - XLTM, which involves "incorporation of small, highly reactive molecules" [56]. Probably this material involves co-polymerization in order to increase the concentration of terminal vinyl groups and establish the required crosslinking network at lower irradiation dose.

After synthesis, the polymer powder requires no purification, except removal of slurry diluents in a staggered drying process.

It is difficult to measure the molecular weight of PE-UHMW because the long polymer chains are too entangled to permit measurable shear flow. Dilute solution viscosity [57] must be used to measure average molar mass. The intrinsic viscosity IV is determined and the viscosity average molecular weight M_v is calculated using Mark- Houwink- equation [24,58]. PE-UHMW auto-crosslinks during processing by heat and pressure. The degree of autocrosslinking is low, but it inhibits complete dissolution of the polymer in hot solvent. Hence, solution technique is not applicable anymore [2]. Alternative methods for molecular weight characterization are melt rheometry [59], sequential extraction and gel permeation chromatography (GPC) [24]. In Figure 8 the molecular weight distribution of GUR 1020 determined by GPC is indicated. Due to inherent solubility problems, the high molar mass fractions are probably under-represented [60].



Figure 8: Molecular weight distribution of GUR 1020 determined by GPC; $M_n = 4.3 \times 10^5$ g/mol, $M_w = 1.9 \times 10^6$ g/mol, $M_z = 3.7 \times 10^6$ g/mol [24]

The PE-UHMW nascent reactor powders have a high degree of crystallinity and (artificially) high average lamellar thickness, which can be attributed to a weird morphology of reactor powder [58,61,62]. In Table 2 the thermal properties of GUR 1050 powder are shown.

Morphology, average size, and size distribution of the PE-UHMW reactor powder particles vary with producing company [28]. This can be attributed to different catalyst systems and polymerization conditions [24].

Table 2: Results from DSC measurements of GUR 1050 powder: T_{m1} – melting point in the first heating run, T_{m2} – melting point in the second heating run, T_c – minimum temperature during crystallization, $T_{c, onset}$ – temperature at the beginning of the crystallization, $X_{DSC, 1}$ – degree of crystallinity calculated from the first DSC heating run, $X_{DSC, 2}$ – degree of crystallinity calculated from the second DSC heating run, I_c – mean lamellar thickness calculated from the first heating run

T _{m1} (°C)	T _{m2} (°C)	T _c (°C)	T _{c, onset} (°C)	X_{DSC1} (%)	X_{DSC2} (%)	l _c (nm)
141.7 ± 0.1	132.8 ± 0.2	119.8 ± 0.2	122.7 ± 0.0	71.5 ± 1.0	53.8 ± 1.4	79.5 ± 1.8

2.2.2 Differences types of PE-UHMW used for total joint replacement

PE-UHMW powder is classified in three Types (Type 1, 2 and 3) by ASTM F 648 [63]. The types have different molar mass and material properties (in terms of ash, trace element concentrations, and mechanical properties of fabricated form). No stabilizers or processing aids are to be added to the polymer powder during manufacture [63]. Virgin PE-UHMW polymer powder meeting the requirement of ASTM F 648 [63] can be blended with α -tocopherol (vitamin E). According to ASTM F 2695 [64], the content may be based on the agreement between vendor and purchaser. No other stabilizers or processing aids are to be added to the virgin polymer powder. Requirements on fabricated forms containing vitamin E are the same as the ones given in ASTM F 648 [63].

Virgin powder and fabricated forms meeting the requirements of ASTM F 648 [63] can be crosslinked with gamma and/or electron beam ionizing irradiation greater than 40 kGy (for the purpose to generate crosslinks within the polymer). The manufacture of crosslinked UHMWPE material may be accomplished with many proprietary methods (see 2.2.4). The end result of this variation is that some of the mechanical properties of crosslinked PE-UHMW exhibit a wide range of values. Coupled with the fact that the limiting value for any specific mechanical property necessary for clinical success is yet unknown, only suitable standard methods for characterizing these material states are given in ASTM F 2565-06 [65].

Finally, ASTM F 2759-09 [66] gives guidance on the assessment of PE-UHMW components in orthopedic device. The standard gives suitable methods concerning the assessment of physical and mechanical properties, wear behavior and biocompatibility [66].

Currently there are several PE-UHMW polymer powder grades on the market which meet the requirements of ASTM F 648 [63]. The most employed grades are produced by Ticona (Oberhausen, Germany). They produce Type 1 polymer – GUR 1020 and Type 2 polymer – GUR 1050. Basell Polyolefins (Wilmington, Delaware, USA) produced a Type 3 polymer – 1900. The production was discontinued 2002, but this material type is still in use [28]. DSM (The Netherlands, Europe) brought a Type 3 polymer – MG003, to the market recently. An overview is given in Table 3. Ticona as well as DSM offer their PE-UHMW medical grades already blended with Vitamin E (typical concentration: 0.1 %wt vitamin E added) [56,67].

	standard	GUR 1020	GUR 1050	GUR 1020	GUR 1050	MG 003
molar mass M_v (10 ⁶ g/mol)		3.5	5.5 - 6	3.5	5.5 - 6	8
concentration of vitamin E (wt%)				0.1	0.1	
viscosity number (ml/g)	ISO 1628-3	2400	3600	2400	3600	
density (kg/m ³)	ISO 1183	0.93	0.93	0.93	0.93	0.938
impact strength (Charpy) (kJ/m ²)	ISO 11542-2	230	170	230	170	60
impact strength (Izod) (kJ/m ²)	ASTM F 648	130	80	≥ 126	≥73	

Table 3: Overview about PE-UHMW polymer powder used in total hip replacement – properties of virgin powder and fabricated form; according to information brochures from Ticona [67] and DSM [56]

2.2.3 Consolidation of PE-UHMW

PE-UHMW has a very high melt viscosity (app. 10^{10} Pa s, compared to melt processed polymers: $10^4 - 10^6$ Pa*s). If PE-UHMW is subjected to standard high shear consolidation methods (i.e. injection molding, screw extrusion or blow molding) the polymer molecules undergo chain scission to the extend that final mechanical properties are reduced [2]. Commonly, two consolidation methods are used: ram extrusion and compression molding. Both methods are employed for PE-UMW used in total hip replacement [64].

The governing mechanism is self-diffusion: PE-UHMW chains in adjacent polymer particles intermingle at molecular level. As diffusion limited process, consolidation of PE-UHMW requires sufficient time at elevated temperature and pressure. Additionally, PE-UHMW exhibits a strikingly slow meting behavior [68]. Nevertheless, consolidated PE-UHMW retains a memory of its prior granular structure [28].



Figure 9: Consolidation of PE-UHMW: compression molding (left) and ram extrusion (right)

Compression molding involves a hydraulic press with a mold containing conduits for oil (heating) and water (cooling), see Figure 9, left. The mold is evenly filled with PE-UHMW powder and closed. The polymer particles are then subjected to a pressure and temperature program. Ticona advices [69] to compact the polymer particles with a pressure of 70 - 100 MPa. The mold is heated till the polymer sheet core temperature is 190 - 200 °C (temperature of the mold should be 10 °C higher than the aimed core temperature of the polymer sheet), the pressure is reduced to 50 bar. Heating should last 1 hour per 10 mm plate thickness. Cooling should last app. 50 % of the time of heating and the pressure is elevated to 100 MPa again. Commercially, the process can last up to many hours [28,70].

At laboratory scale DIN EN ISO 11542-2:2010 [71] suggests a temperature of 210 °C, cooling rate of 15 °C/min and pressure of 10 MPa for 30 min. This consolidation process should be used for specimen preparation. Similar procedures concerning temperatures, pressure and processing times are published by [72, 2]. Direct compression molding offers the possibility of producing semi-finished parts pressing the polymer powder in indivual molds [69]. But most manufacturers of implants use bulk consolidated PE-UHMW material (produced by a converter) [28].

The quality of the final part is determined by even filling of the mold – if there are local differences in powder density, the material is subjected to (local) shear under pressure resulting in stresses within the part and mechanical degradation in the worst case [72]. The application of temperature during heating is crucial since the material is not protected against oxidative degradation. Cooling rate and applied pressure influence the degree of crystallinity [72].

The other consolidation method frequently applied is ram extrusion: The polymer powder is feeded into a cylinder. A hydraulic ram moves along this cylinder. The powder is compacted and moved through the cylinder from the feed to the die. During this process the compacted powder passes three heating zones (temperatures: 160 -180 °C, 220 °C, 160 -180 °C) [69]. The process is pictured in Figure 9, right. Typically this process produces 5 - 10 kg rod per hour. During ram extrusion the polymer powder and the highly viscous melt are subjected to shear at the cylinder wall [73].

Historically, GUR 1020 has been compression molded and GUR 1050 ram extruded [24]. The description of the consolidation methods suggests the properties of PE-UHMW are affected by the consolidation method. Nevertheless, differences in the bulk properties are low between contempory compression molded and ram extruded GUR PE-UHMW. A survey by Kurtz [28] revealed that consolidated GUR PE-UHMW Type 1 and 2 exceed requirements of ASTM F 648 [63]. Density is significantly affected by powder type not by consolidation method, whereas impact strength and tensile properties are significantly affected by powder type and consolidation method. Bellare et al. [73] compared morphology of ram extruded rod and compression molded sheets. Both material states show low crystallographic texture. In the outer circumference of the ram extruded rod the crystallites had a preferred orientation whereas in the centerline they show random orientation. This is explained by crystallization from oriented melt – shear forces align polymer chains parallel to the cylinder wall. In compression molded sheets the melt is oriented too. The chains align perpendicular to the direction of compression and crystallize accordingly.

In order to enhance particle cohesion in compression molded PE-UHMW by chain diffusion across fusion boundaries Fu et al. [74] investigated the effects of high temperature melting after consolidation on structural parameters and mechanical properties. High temperature melting at 280, 300, and 320 °C resulted in massive chain scission, self-diffusion (chain entanglements across the granule boundaries are enhanced), and increased crystallinity leading to improved tensile and impact properties of the material. The yield strength, ultimate tensile strength and the wear rate were not significantly affected.

2.2.4 Crosslinking and thermal treatment of PE-UHMW liners

The next step in manufacturing of orthopedic implants is crosslinking. Crosslinked PE-UHMW is used in total hip endoprosthesis in order to reduce wear *in vivo* and hence, prolong longevity of the implant (see 2.1).

Generally, PE-UHMW can be crosslinked by ionizing radiation, chemically induced by peroxides or silane compound induced [10]. In orthopedic application only radiation induced crosslinking is employed [65]. The gamma-irradiation and electron beam technique use different technologies. During gamma-irradiation packages of the products are moved around a

radiation source (Co^{60} or Cs^{137}) until the minimal dose is reached at every point of the product. Nowadays, the precision of dose application is maximum dose/minimum dose ≥ 1.1 because of sophisticated movement around the gamma-source [75]. Electron beam technology uses accelerators with different energy (determines penetration depth) and power (determines capacity). The product is moved with a certain velocity through the e-beam (eventually the procedure is repeated until the required dose is deposited). The penetration depth is much higher with gamma-rays than with electron beam (Figure 10, left). Hence, with e-beam technology the product is irradiated from e.g. two sides [76] in order to increase homogeneity of absorbed dose and precision of dose application (see Figure 10, right). Velocity of energy transfer is different in both technologies. In approximation, gamma radiation requires 100 hours to transfer 100 kGy, whereas e-beam transfers 100 kGy within 10 seconds [77]. Generally, penetration depends on the density of irradiated material (1 Gy corresponds to 1 joule/kg) but the density of the PE-UHMW material states used in orthopedics is practically the same.



Figure 10: Dose-depth profiles: comparison of penetration depth gamma- and electron beam technology (left), increase in penetration homogeneity and precision in electron beam technology (right); adapted from [75]

PE-UHMW is irradiated by gamma-radiation or electron beam with the purpose of generating crosslinks in the material (dose > 40 kGy [65]) or sterilizing final components (dose 25 - 40 kGy). The interactions of the polymer with ionizing radiation are the same. They are largely affected by the conditions during and after irradiation. If PE-UHMW is irradiated, chain scission and crosslinking occur simultaneously. If oxygen is present chain scission dominates, under inert atmosphere crosslinking dominates. In any case long living radicals are generated. These radicals react with oxygen during the service time of the implant and lead to oxidative degradation of the material. The chemical mechanisms are described in 2.4.1.

The crosslink density increases with increasing radiation dose up to a saturation level at around 100 kGy. The wear rate decreases with increasing irradiation and reaches a plateau at around 100 kGy (see Figure 11) [78].

The precise mechanisms why crosslinking improves wear resistance are not completely understood. The improved wear behavior is assumed to come from the higher resistance to orientation that accompanies crosslinking (see 2.4.3) [79]. The dominant wear mechanism for polyethylene in hips involves preferential orientation, followed by debris formation due to cross-shear. Crosslinking makes it more difficult for the material to become oriented preferentially [79,80].



Figure 11: Wear rate as a function of radiation dose in cold irradiated and subsequent melt PE-UHMW; data from bi-directional pin-on-disk test [78]

In crosslinked PE-UHMW the concentration of radicals after irradiation is reduced by subsequent thermal treatment [81]. Hence, the material is somewhat stabilized against oxidative degradation. Many methods have been developed for crosslinking PE-UHMW in orthopedic applications. They aim is to find an optimum between oxidative stability, mechanical properties (especially resistance to crack initiation and crack growth), and wear behavior *in vivo*. Currently a second generation of crosslinked PE-UHMW is in clinical use [13,20].

The crosslinked PE-UHMW implants are manufactured by starting with pre-forms of consolidated PE-UHMW. These pre-forms are irradiated either with gamma-irradiation or electron beam at ambient or elevated temperatures. Both irradiation procedures introduce crosslinks in the polymer and as a consequence the plastic deformation and fracture toughness is reduced [18].

Stabilizing treatments involve remelting or annealing. Remelting is effectively reducing residual radical concentration below a measurable level. Hence, the material is better stabilized against oxidative degradation but the degree of crystallinity is lower resulting in decreased strength and increased compliance (which is favorable in load bearing applications as the contact stress is reduced) [82].

Thermal annealing preserves the microstructure but is less effective in quenching free radicals. Hence, the mechanical properties, like yield strength and ultimate tensile strength are better than in crosslinked and remelted PE-UHMW, but the resistance against oxidative degradation is worse [83].

The reduced fracture toughness and oxidative stability is accepted with regard to the clinical benefit obtained from enhanced wear resistance due to crosslinking. Nevertheless, there is still potential in optimization of the properties of crosslinked PE-UHMW in endoprosthesis systems as the rim fractures reported by Furmanski et al. [44] show.

Most highly crosslinked material modifications are developed by scientists in charge of a orthopedic manufacturer or in collaboration with a manufacturer. Therefore, studies directly comparing the properties of hip implants produced by different manufacturer are rare. The data measured by Collier et al. [81] regarding first generation crosslinked PE-UHMW hip implants is summarized in Table 4 and supplemented by data concerning $X3^{TM}$ form Morrison at al. [84].

Finally, the implants are manufactured, packed and sterilized. These procedures are similar in crosslinked and non-crosslinked PE-UHMW implants. They are discussed in 2.2.5 and 2.2.6.

An overview about state of the art manufacturing procedures for crosslinked PE-UHMW is given in Figure 12.

Table 4: Comparison of structural parameters and mechanical properties of crosslinked PE-UHMW [81]; * advertised wear rate reduction percentages. The wear rates were not measured with a consistent, standardized method. The material states used as benchmarks by the individual companies differ. Therefore, the wear reductions reported are not necessarily comparable; ° X3 was not included in the study by Collier et al. [81], data from Morrison at al. [84] and [83]

crosslinked material	OI (-)	crystallinity (%)	free radical concentration (mol/dm ⁻³)	yield strength (MPa)	UTS (MPa)	elongation (%)	wear rate reduction* (%)
ArComXL®	$\begin{array}{ccc} 0.042 & \pm \\ 0.032 \end{array}$	64 ± 8.9	3.8 x 10 ⁻⁴	24 ± 0.8	59 ± 4.7	240 ± 38	42
Marathon TM	$\begin{array}{ccc} 0.005 & \pm \\ 0.004 \end{array}$	43 ± 1.9	n.d.	21 ± 0.5	56 ± 7.0	300 ± 14	85
XLPE TM	$\begin{array}{cc} 0.007 & \pm \\ 0.004 \end{array}$	44 ± 3.0	n.d.	20 ± 1.3	56 ± 7.1	300 ± 20	86
Crossfire TM	$\begin{array}{ccc} 0.036 & \pm \\ 0.030 \end{array}$	58 ± 5.2	7.3 x 10 ⁻⁴	22 ± 1.0	53 ± 5.3	230 ± 17	90
Durasul®	$\begin{array}{ccc} 0.072 & \pm \\ 0.027 \end{array}$	44 ± 4.1	n.d.	19 ± 1.6	34 ± 3.4	330 ± 19	100
Longevity TM	$\begin{array}{ccc} 0.004 & \pm \\ 0.002 \end{array}$	44 ± 1.3	n.d.	21 ± 1.1	43 ± 5.3	250 ± 50	90
X3 TM °	$\begin{array}{cc} 0.100 \ \pm \\ 0.030 \end{array}$	62 ± 1.1	0.73 ± 0.16 x10 ¹⁵ spins/g	23 ± 0.2	48 ± 3.2	267 ± 17	79
PE-UHMW	$\begin{array}{ccc} 0.022 & \pm \\ 0.008 \end{array}$	61 ± 4.6		22 ± 1.0	58 ± 4.7	380 ± 10	

GUR 1050 compression molded	65 kGy e-beam bei 120 °C	remelting 150 °C, 2 h		milling	gasplasma		Prolong (Zimmer)	R 1050 isostatic pression molded) kGy gamma	anical annealing state extrusion) mal annealing 130 °C	milling	gasplasma	弁	ArCom XL (Biomet)
	00 kGy e- m bei 40 °C	emelting 50 °C, 6 h		milling	asplasma		ongevity™ Zimmer)	GUF	20	mech (solid ther				
	1(beal	- 47			ő		C C		nma	ping" ffusion) 0 °C		Ima		Щ
	95 kGy e-beam bei 120 °C	remelting 150 °C, 2 h		milling	ethylenoxid	5	Durasul® (Zimmer)		100 kGy gan	Vitamin E "do (accelerated dif annealing13	milling	30 kGy gam in Argon	'≓>	ePoly HXLI (Biomet)
	100 kGy gamma	itamin E "doping" celerated diffusion)	Innealing 130 °C	milling	30 kGy gamma in Argon		ePoly HXLPE (Biomet)	GUR 1020 ram extruded	30 kGy gamma	3 times sequentially annealing 130 °C, 8 h	milling	gasplasma		X3 TM (Stryker)
		(ac	σ						nma	p 4		xid		M ohew)
	Gy gamma	ting 155 °C, h, red. O ₂	aling 120 ്ഗ h, red. O ₂	milling	asplasma	ť	arathon™ DePuy)		75 kGy ga	remeltir 147 °C,	milling	ethyleno	4	XLPE ¹ (Smith&Ne
	50 k	remel 24	anne 24		ge		Ξ		nma	5 °C, 02 °C 02 °C		la		(
GUR 1050 ram extruded	100 kGy gamma	remelting 147 °C, 5 h		milling	ethylenoxid	-2-	XLPE TM Smith&Nephew)	JR 1020 extruded	75 kGy gan	remelting 15 24 h, red. annealing 12 24 h, red.	milling	gasplasm	€	AltrX (DePuy
	75 kGy gamma	annealing 130 °C]	milling	30 kGy gamma in N ₂ /Vak.	-	Crossfire TM (Stryker)	GU	50 kGy gamma	remelting 155 °C, 24 h, red. O ₂ annealing 120 °C 24 h, red. O ₂	milling	gasplasma	ŧ	XLK (DePuy)

Figure 12: Manufacturing of highly crosslinked PE-UHMW implants currently in clinical use, according to [10,13,24,28,39,81-83]; material states highlighted blue are used in total hip joint replacement, material states highlighted red are used in total knee joint replacement and material states highlighted blue and red are used in total hip and knee replacement

2.2.5 Manufacturing of PE-UHMW liners

Orthopedic manufacturers machine consolidated PE-UHMW or crosslinked pre-forms into the final implant. The exact manufacturing techniques are naturally proprietary of the manufacturer, but consist of milling and turning operations for roughing and finishing steps [24]. The mechanical tolerances for hip implants are close [85]. Hence manufacturing processes have to be well controlled. Feed rate, tool cutting force and spindle speed have to be closely monitored since excessive heat and mechanical stress damages the PE-UHMW [28]. The surface finish varies with orthopedic manufacturer and material state (Figure 13).



Figure 13: Machining marks in non-polished region of irradiation sterilized PE-UHMW explant after 58 months *in vivo* (up left), virgin implant made from X3 (up right) and Durasul® explant after 9 days *in vivo* (down middle);

The machining marks determine surface roughness of the final product. Hence, they influence the initial wear rate, whereas the roughness of the hard counterpart determines long-term wear rate [24]. But little is known about the effect of machining parameters on tribological performance of PE-UHMW [28].

The machining marks determine the optical and haptical appearance of the implant. They evoke feelings related with the quality of the implant.

After milling the implants are cleaned, packaged under controlled environment and labeled. The choice of packaging system is based on the final sterilization method.

2.2.6 Sterilization of PE-UHMW liners

Like any other implant, PE-UHMW hip liners have to be sterilized prior to implantation. Heat sterilization methods [86] are not applicable due to dimensional instability of PE-UHMW at the specified sterilization temperatures.

Irradiation sterilization with gamma radiation and electron beam as well as gas sterilization with ethylenoxid and gas plasma are currently applied (see Figure 12).

Using the first two methods, the PE-UHMW is subjected to ionizing radiation at doses levels of 25 - 40 kGy [65]. The sterilization was performed in air by the majority of hip implant manufacturing companies from the late 1960s until 1995. Many studies [21,22,87] demonstrate the adverse effect of this procedure due to (massive) oxidative degradation during shelf storage and *in vivo* use. Contemporary irradiation sterilization is performed under reduced oxygen atmosphere (nitrogen, argon, or vacuum) in barrier packaging. This method protects the liners

against oxidative degradation during shelf aging (as far as the packaging system works well over time). As soon as the implants comes in contact with oxygen (e.g. from the synovial fluid), the residual free radicals react and auto-accelerating oxidative degradation starts (see 2.4.1) [88,89]. Gas sterilization procedures are surface sterilization methods [86] and performed in gas permeable packaging.

The methods do not alter structure and properties of PE-UHMW [25-27]. No radicals are generated. Hence, no precursors to oxidative degradation are in the material [22] and adversely, no low level of crosslinking is introduced to the PE-UHMW. Directly after sterilization the wear behavior of ethylene oxide sterilized PE-UHMW is worse compared with gamma-irradiated PE-UHMW [90,91]. This observation is reversed after aging - gamma-irradiated PE-UHMW underwent higher wear than the EtO-sterilized PE-UHMW [91]

2.3 Influence of in vivo use on PE-UHMW

The success of endoprothesis systems and the materials used is determined by *in vivo* performance. There are three approaches in evaluating *in vivo* success.

First, clinical observation: general health and mobility of the patients as well as the wear behavior are monitored over years.

Second, statistics based on data from implant registries, i.e. nation wide population is covered. These evaluations give information on the performance of a prosthesis design or a material modification compared with other designs or material modifications, the influence of surgical techniques (e.g. cemented or uncemented hip athroplasty), population based and regional differences. Further, differences in the success of total hip replacement related to age, gender, insurance system, and other gathered parameters can be elucidated [37,92]. The registries help to become aware of problems with e.g. a certain endoprosthesis system, at an early stage and help to protect the patients.

The third approach covers scientific investigation of retrieved implants. The number of implants investigated in these studies varies e.g. between 4 and 47 [23,44,45, 93-99]. The influence of *in vivo* use is investigated with many methods, but the conclusions are complicated by the fact that the initial state of the implants is not known.

The variety of material states currently implanted complicate evaluation of the success of specific material improvement(s). During *in vivo* use the material is subjected to individual mechanical and biochemical stresses. The success in terms of prolonged *in vivo* survivorship can be determined years after implantation only. Hence, a great number of explants have to be examined in order to gain statistically significant conclusions on the success. Additionally, the material states can be employed in different endoprosthesis design over time. Without generation of an implant register covering as many patients as possible evaluation of material improvement is not reasonable probably. In the end this may limit new material developments and include risks for the patients.

Some general considerations about the influence of body environment on the functionality of the total joint replacement are:

In the human body the temperature of the articulating joint during walking was shown to be maximum 43.1 °C and it seems likely that the temperature could be higher [100].

An important aspect of application within the body is the surrounding media. Similar to the natural joint, the artificial joint is lubricated by a body fluid (synovial fluid), which contains water, proteins (e.g. albumin, γ -globulin), lipids, phospholipids, glucose and hyaluronate [101]. Because synovial fluid itself cannot be extracted in larger amounts, in aging experiments often diluted buffered saline solution is used to simulate body fluids [102]. In the field of wear testing calve serum diluted with deionized water is used to substitute synovial fluid [103]. In fatigue studies deionized water at 37 °C respectively 40 °C [26,104,105] or different

concentrations of hyaluronate in bovine serum [101] are used to simulate body environment. Nevertheless, it is a scientific concern if the *in vitro* tests reflect *in vivo* conditions adequately.

Pure polyethylene is not biodegradable, whereas oxidized polyethylene (e.g. resulting from manufacturing processes and aging) is biodegradable by *in vivo* processes [21].

Presumably changes in the mechanical properties of the material due to the adsorption of lower mass molecules from surrounding media occur. Costa et al. [106] showed the increase of ester groups due to adsorption from body fluids on retrieved components. The effect of lipid adsorption on the uniaxial compressive properties was investigated by Greenbaum et al. [107]. It was shown that the mechanical properties were adversely affected by the lipid uptake.

Protein adsorption from the synovial fluid on the PE-UHMW is non-specific. Adsorbed proteins influence lubrication [108].

Wear assessment focuses on walking. But the patients have different actives in every day's life [54]. Some of them result in very high peak loading of the implant [109].

2.4 Structural parameters of PE-UHMW at different levels

The structure of PE-UHMW covers many length scales: Molecular dimensions are below nm size (around 10^{-1} nm), crystal lamellae are typically in the range of 20 - 80 nm, and the spatial arrangement of the lamellae leads to a microscopic pattern. This structure development is hierarchically organized: the molecular constitution influences the morphology. Furthermore, both parameters are influenced by thermal and mechanical treatment of the material during life cycle. An overview about the structural parameters at the different levels is given in Table 5. The parameters and their interdependencies are discussed in 2.4.1 - 2.4.3.





2.4.1 Molecular level

PE-UHMW is a homopolymer synthesized by Ziegler-Natter polymerization (see 2.2.1 and 2.2.2). Without further physico-chemical treatment it is a linear chain with small amounts of irregularities (mainly vinyl double bonds). It consists of CH_2 - groups (polymer chain backbone), CH- groups (at branching points, very low concentration), and C=C- groups (vinylene group) [110].

If the polymer chain is subjected to energy higher than the energy of the C-C bond (thermal or radiation energy) macroradicals are generated (Scheme 1, reaction 1). The reactions in absence of oxygen are shown in Scheme 1.

Primary macroradicals (Scheme 1, reaction 2) recombine immediately (Scheme 1, reaction 3) due to limited mobility of the polymer chain. Hence, primary radicals are not detected in PE-UHMW [111].

In reaction 4 (Scheme 1) a secondary macroradical and an H radical are formed. The H radical is highly mobile and can extract an H atom intra-molecular (Scheme 1, reaction 6) or intermolecular (Scheme 1, reaction 7). A trans-vinylene double bond and another secondary macroradical are generated respectively. Additionally, recombination reaction (Scheme 1, reaction 5) becomes less likely. Furthermore, the alkyl-radical site can migrate along the polymer chain via H transfer. If a vinylene group is reached a thermodynamically stable allyl-radical is formed [110].

A secondary macroradical can react with terminal vinyl bond (Scheme 1, reaction 8). A Ycrosslink is formed. Other vinylene groups do not react due to steric hindrance. In the solid the formation of H-crosslinks (Scheme 1, reaction 8a) is impossible in the crystalline phase and unlikely due to steric hindrance. The presence of H-crosslinks has been ruled out by NMR studies in polyethylene irradiated in the solid state [112]. Experimental data show that the level of crosslinking increases with irradiation dose and reaches a plateau at around 100 kGy, when the majority of the terminal vinyl double bonds have been consumed [110 111,113,114]. After irradiation in the molten state H-crosslinks have been proved by NMR studies [112].



Scheme 1: Radical reactions in irradiated PE-UHMW in the absence of oxygen (adapted from [111])

Thermodynamic feasibility of a reaction is independent from the phase (i.e. crystalline or amorphous). The same reaction can or cannot be kinetically favored depending on temperature, physical state (e.g. melt), and phase. Kinetics depends on temperature, steric hindrance and chain mobility [110]. Furthermore, the reactions depend on the statistical probability of collision of the reactants (i.e. concentration, chain mobility and diffusion) [115]. These

considerations are one basis of commercially crosslinking procedures described in 2.2.4. For example irradiation at elevated temperature reduces degree of crystallinity and enhances chain mobility, remelting enables crosslinking reactions of entrapped macroradicals from the crystalline phase otherwise sterically hindered, and annealing enhances chain mobility.

Secondary macroradicals react with oxygen dissolved in the amorphous phase of bulk polymer and diffused into the polymer from surrounding environment [9,27,116]. The mechanism of oxidation of hydrocarbons, known as Bolland's cycle, was studied in liquid phase at 70 - 80 °C. PE-UHMW in solid phase at room temperature exhibits reduced chain and macroradical mobility, different kinetics and diffusion rates of oxygen. Therefore, a modified Bolland's cycle is proposed by Costa et al. [111] (shown in Scheme 2).



Scheme 2: Oxidative degradation cycle in PE-UHMW [111]

In post-irradiation oxidation the radicals are formed by high energy radiation, whereas in thermo-oxidation they are formed due to decomposition of peroxides (> $80 \,^{\circ}$ C). The formation of ketons is dominated by reaction 9 and 10 (Scheme 2) in post-irradiation oxidation and by reaction 17 in thermo-oxidation. Nevertheless, the same oxidation products (hydroperoxides, ketons, acids, and alcohols) and their same relative abundance were result from thermo-oxidation and post-irradiation oxidation [111].

Secondary alkyl-macroradicals decay early after irradiation. Due to intra 1-5 or 1-7 and intermolecular hydrogen transfer thermodynamically stable allyl- macroradicals are generated in the amorphous phase. The rate of decay is slower in the crystalline phase due to restricted chain mobility leading to kinetically unfavored 1-2 hydrogen transfer [110]. It is further suggested that the long-lived oxygen-induced radicals in PE-UHMW are present at least up to 15 years [117,118]

Mechano-oxidative degradation is pictured in Scheme 3 [119]. It involves the generation of primary macro-radicals which react with oxygen (Scheme 3, reaction 21) and form ester groups (Scheme 3, reaction 22 and Scheme 2, reaction 12) and acids (Scheme 3, reaction 23). In mechano-oxidation, the resulting oxidation products as well as their relative abundance differ from thermo- and post-irradiation oxidation [77,119].



Scheme 3: Mechano-oxidative degradation of PE-UHMW (adapted from [120])

The mechanisms of oxidative degradation of PE-UHMW polymer chains lead to polymer embrittlement [20, 27, 120-126]. The processes reduce the molar mass and lead to worse mechanical properties [20,124]. The dose-depth profile resulting from the irradiation procedures together with diffusion processes of oxygen in the PE-UHMW (possible during irradiation, shelf aging and/or *in vivo* use) lead to the so called white band region [122, 125]. In this region the polymer is highly oxidized [126] and sample preparation processes like cutting, microtoming, and grinding lead to the formation of micro-cracks which are visible to the naked eye as white band [121]. This subsurface area can not be attributed to subsurface fatigue since it was observed in irradiated, shelf aged virgin implants [120], non-tested three point bending specimen [121], and in e.g. non-tested tensile specimen.

In standard PE-HD material the auto-accelerating oxidation cycle is inhibited by additives (antioxidants). In PE-UHWM for orthopedic applications vitamin E can be used as antioxidant (see 2.2.2). Vitamin E (α -tocopherol) is an antioxidant, whose main role *in vivo* is to stabilize the active free radicals resulting from the oxidation of polyunsaturated fatty acids in cell membranes [127]. This natural compound and its decomposition products are biocompatible [11]. In PE-UHMW the vitamin E is spread in the amorphous phase and its mobility is restricted due to its low diffusion coefficient (at room temperature) [115]. It acts as a radical scavenger (chain breaking donor) and reacts with a secondary macroradical or a peroxiradical [115]. In this reaction, the vitamin E (Figure 14, a) is consumed and becomes a kinetically stable radical itself (Figure 14, b). Vitamin E has been proven to be a very effective antioxidant in PE-UHMW for orthopedic applications [115,127-130].



Figure 14: Chemical structure of (a) α-tocopherol, i.e. vitamin E and (b) α-tocopheryl radical [127]

As vitamin E reduces the concentration of secondary radicals, the irradiation of PE-UHMW blended with vitamin E results in a lower degree of crosslinking [130] but it protects the material from oxidative degradation during the whole manufacturing process. An alternative method for incorporating vitamin E in PE-UHMW is doping (accelerated diffusion or diffusion

with supercritical CO₂) [128]. Combinations of blending and diffusion processes offer the possibility of gradient crosslinking PE-UHMW. PE-UHMW with high degree of crosslinking on the surface and low degree of crosslinking in bulk material offers high wear resistance, oxidative stability and improved fatigue resistance [131].

In a recently published study by Gallardo et al. [132] europium stearat was successfully used as antioxidant. Addition of europium stearat increased oxidation stability of PE-UHMW and enables polyethylene wear to be traceable in body fluids.

2.4.2 1st supermolecular level: crystalline and amorphous phase

PE-UHMW is a semicrystalline polymer in the solid state. At nanometer scale it has three regions: crystalline phase, amorphous phase and interphase between both.

The crystallites are built by chain folding of polyethylene molecules. The most stable crystal structure is the orthorhombic unit cell. Two meta stable crystal structures exist: the monoclinic unit cell – in samples subjected to mechanical stress [133], and the hexagonal unit cell – in samples crystallized under high pressure and during crystal growth [134]. Chain folded crystals are not in thermodynamic equilibrium. The non-equilibrium state itself depends on the thermal history (e.g. thermal conditions during crystallization, annealing ...) of the material [135]. Usually the degree of crystallinity is 45 - 60 % in PE-UHMW [70,10].

At the interface between crystal and amorphous phase there is an all-trans phase. In PE-UHMW this all-trans phase can be e.g. 30 wt% in virgin, consolidated GUR 1020 and it declines upon irradiation and aging by transforming in crystal phase [70].

Since no crystal structure is observed although the chains are in all-trans conformation, most of this phase is added to amorphous phase (depending on the method used for investigation - Raman spectroscopy, NRM, and small angle X-ray scattering (SAXS) allow investigations on the interfacial component [133]).

The amorphous phase is the rest (around 20 wt% [70]) – all structural irregularities of the polymer chain itself (e.g. crosslinks, oxidation products, branching points ...), residuals of the catalyst, the additive (i.e. vitamin E), entanglements (physical crosslinks), and non-ordered segments of the polymer chain. The density of the amorphous phase is lower than the density of the crystalline phase.

Intercrystalline molecular connections largely influence the mechanical behavior of semicrystalline polymers. In particular, they influence toughness and long-term behavior of polyethylene materials [136]. These intercrystalline molecular connections hold the crystallites together by covalent bonds (otherwise only weak van der Waals – interactions would keep them together). Two species of mechanically active (load transferring) molecules exist: the tie molecules - running from the crystalline phase through the amorphous phase and again in the crystalline phase, and chain entanglements - connecting two macromolecules sticking in different crystallites via loops [136-138].

The morphology of PE-UHMW on the 1^{st} supermolecular level is pictured in Figure 15.



Figure 15: Morphology of a semi-crystalline polymer like PE-UHMW at molecular level. l_c ... average lamellar thickness, l_a ... average thickness of amorphous phase

Structural parameters characterizing morphology at nanometer scale are the long period l_p , average lamellar thickness l_c and average thickness of amorphous phase l_a (see Figure 15). Direct evaluation of tie molecules and entanglement is not possible. Hence, indirect methods are employed. An overview about this topic is published by R. Seguela [136]. One approach is the assessment of intercrystalline molecular connections by their influence on mechanical properties [139]. The other approach is the theoretically assessment of tie molecules and entanglements ob the basis of statistical mechanics of polymer molecules [136]. The basis of this approach is the probability of tie molecule formation in an isolated chain P given by:

$$P = \frac{\int_{l_{T}}^{\infty} r^{2} e^{-b^{2}r^{2}} dr}{3\int_{0}^{\infty} r^{2} e^{-b^{2}r^{2}} dr}$$
(1)

Equation (1) is proposed by Huang and Brown [137] and it is based on Gaussian statistics for chain segments of a freely jointed chain in three dimensions by Flory [140]. A single chain at the moment of crystallization is considered [136]. If the end-to-end distance of the random coil of the polymer chain is greater than $l_T = 2l_c + l_a$, a tie molecule will be formed. The mean square value of the end to end distance is given by:

$$r^2 = C \cdot x \cdot l^2 \tag{2}$$

With C the chain extension factor (accounts for non-freely jointed chain as a real chain has certain valence and rotation angles), a constant with the value 6.8 in polyethylene, x the number of links (determined from molar mass of the polymer chain [141]) and I the link length, 0.153 nm (C-C bond length in polyethylene) [142].

The probability of a given end-to-end distance is given by [140]:

$$p(r) = d \cdot r^2 \cdot e^{-b^2 r^2} \tag{3}$$

With the factors d and b is determined by [140]:

$$d = \frac{4b^{3}}{\sqrt{\pi}}$$
(4)
$$b^{2} = \frac{2/3}{r^{2}}$$
(5)

The factor 1/3 in equation (1) account for the fact that only polymer chains with an end-to-end vector perpendicular to the lamellar surface can build tie molecules as the other two dimensions of the lamella are much larger [137]. This approach provides a molecular explanation of mechanical properties [137,142,143]

The model of Huang and Brown [137] has been further improved. Yeh and Runt [144] considered not only tie molecules but also chain entanglements. The probability of two entangled polymer chains to crystallize in two different lamellae is calculated. The authors assumed that all entanglements in the melt are preserved during crystallization (no distanglement). It turned out that the probability of formation of chain entanglements is much higher than the probability of tie molecule formation [136, 138].

Seguela [136] proposed a model which includes considerations on cross-section tie molecule and entanglement density (the mechanically active species in the material under load) and chain overlapping in real materials. Base on the model of Huang and Brown [137], the probability of tie molecule formation in an isolated chain P can be expressed as ratio between accumulated weights of the tie molecules TM to the total molar mass M:

$$P = \frac{n_{TM}M_{TM}}{M} \tag{6}$$

It is assumed (based on mechanical considerations) that the contour length of the tie molecules is not much different from l_a :

$$M_{TM} = \frac{M_0 l_a}{l} \tag{7}$$

With M_0 the molar mass of a CH₂- group and 1 the link length. With the density of tie molecules per unit of volume δ_V of the amorphous phase:

$$\delta_V = \frac{n_{TM}}{(1 - V_c)V_{coil}} \tag{8}$$

where n_{TM} is the number of tie molecules, V_{coil} is the volume of a polymer chain with molar mass M and radius of gyration R_g in a random coil formation, and V_c is the crystal volume fraction, the density of tie molecules per unit surface δ_s of the crystal-amorphous interface for an isolated chain is given by:

$$\delta_s = \delta_V \cdot l_a \tag{9}$$

It can be easily converted into the tie molecule area fraction per chain:

$$f_s = \delta_s \cdot S_0 \tag{10}$$

with $S_0 = 0.18 \text{ nm}^2$, the cross section area of a single polyethylene stem emerging from the crystal surface.

Taking into consideration interwinded chains in actual material, the overall area fraction of tie molecules is given by:

$$F_s = f_s \cdot R \tag{11}$$

with R being the ratio between the actual density of the material ρ to the apparent density of an isolated chain ρ_{app} :

$$\rho_{app} = \frac{M}{N_A V_{coil}} = \frac{3M}{4\pi N_A R_g^3}$$
(12)

with N_A being the Avogadro constant.

Finally the tie molecule area fraction can be calculated according to:

$$F_s = \frac{P\rho N_A l S_0}{M_0 (1 - V_C)} \tag{13}$$

Similar considerations on entanglements allow calculation of the equivalent tie molecule surface fraction due to chain entanglements $F_{s,e}$:

$$F_{s,e} = \frac{\rho N_A l_a S_o}{M_e (1 - V_C)} \tag{14}$$

Seguela [136] showed that in PE-LLD and PE-HD are more intercrystalline molecular connections due to entangled chains than due to tie molecules.

All models introduced above evaluate the influence of molecular architecture indirectly. The molecular architecture and the molar mass influence crystallization behavior and hence, the values of l_a , l_c , and the degree of crystallinity [138,142]. Furthermore, thermal conditions during crystallization and annealing effects are reflected by the values of l_a and l_c , and the degree of crystallinity too.

No data concerning tie molecules and entanglements have been published for PE-UHMW so far.

Crystallization of polymers includes three steps: nucleation, crystal growth, and relaxation phenomena compared with reorganization during the life time of the material (physical ageing, theoretically the thermodynamic equilibrium is never reached in semicrystalline polymers). There is lost of literature dealing with crystallization of polymers and polyethylene in particular e.g. [68,133]. Investigations of crystallization behavior are conducted from polymer (diluted) solution or polymer melt (technological more relevant).

Upon changes in temperature or pressure, the free energy of the system changes and phase separation is energetically favored. This phase separation proceeds via nucleation (i.e. hexagonal phase in polyethylene). Crystal nuclei appear and dissolve due to statistical fluctuation (a steady state governed by bulk enthalpy and surface energy). Only nuclei above a critical size will grow. The nucleation rate is related to the supersaturation (e.g. supercooling) via Arrhenius approach [145]. Precursor structures with dimensions below the size of a critical nucleus have been found in polymer melts (memory of its former crystalline structures). They complicate the thermodynamics of nucleation. In PE-UHMW ordered domains exist in the melt even at temperatures very close to the degradation point [146]. Fibrillar structures are present up 220 °C, above this temperature they transform into semi-ordered liquid crystalline phase [68]. Nevertheless, the rate of bulk crystallization is nucleation controlled in PE-UHMW [68], where the preordered structures serve as pre-existing nucleation sites [146].

Above a critical molar mass, the polymer chains are entangled in the melt. These entanglements are essentially preserved during crystal growth. These entanglements and irregularities in molecular architecture of polymer chains are excluded from crystalline phase. According to Fisher's solidification model several lamellae can grow within the sphere of gyration of a sufficient long polymer chain [136]. Hoffman et al. [68] describe crystal growth as a process where polymer chains build up the crystal by attaching to growing crystal surface like zippering down in a niche and chain folding accompanied with reptation (snake-like large-scale motion of the entangled polymer chain). In PE-UHMW the molecules are so long, that many become involved in a nearby lamella or fairly distant points in the same lamellae during crystallization. A situation is created where steady state reptation is nearly impossible and the molecules involved are in a state of tension. The chain folded lamellae are ill-formed and the degree of crystallinity reaches a low level plateau in PE-UHMW (see Figure 16).



Figure 16: Degree of crystallinity at 128 °C as a function of molar mass (adapted from [68])

Initial lamellar thickness is influenced by degree of supercooling during crystallization. Isothermal thickening of the lamellae is influenced again by the temperature, and by time [133]. These effects, together with the chemical architecture of the polymer cause a thickness distribution of the lamellae in the solid material [147].

Chain scission in the solid material as a consequence to irradiation, oxidation and/or mechanical stress causes recrystallization. Already existing lamellae become thicker as freed molecular segments form the inter-facial phase recrystallize [148-150] (see Figure 17) and the degree of crystallinity can increase [150]. The crystal surfaces are tidied up and the crystals get refined [148-150]. In parallel, a second crystal population grows arising form released material too far away from a lamella surface [148,70]. Especially as oxidation proceeds thin crystallites are formed in the amorphous region because of the rearrangement of the polymer chains and the degree of crystallinity rises [150,151]. The increase in degree of crystallinity together with the degradation of tie molecules and entanglements lead to embrittlement of the material [150] and to the loss of mechanical integrity finally.


Figure 17: Effect of irradiation on the degree of crystallinity in PE-UHMW: (a) edge of a lamella with lose loops, (b) chain scissions due to irradiation, (c) recrystallization due to increased mobility of UHMWPE chains; C ... crystalline phase, A ... amorphous phase [149]

2.4.3 2nd supermolecular level: orientations

Due to the very high molar mass in PE-UHMW not spherulites (or axialites) develop in this material [68]. 2nd level supermolecular structure is characterized by crystal lamellae randomly dispersed in the amorphous phase (see Figure 18). Lamellar orientation is induced during consolidation ([73], see 2.2.3) and it is observed upon loading *in vitro* tests [15,80] and *in vivo* [152,153] (see Figure 18).



Figure 18: TEM images of PE-UHMW: (a) bulk GUR 1020; (b) deformed GUR 1020 (parallel to load direction); (c) bulk crosslinked and remelted PE-UHMW; (d) deformed crosslinked and remelted PE-UHMW (parallel to load direction); (e) (f) non-crosslinked PE-UHMW tibial inserts (evidence of a plasticity-induced damage layer); adapted from [15,153]

Lamella orientation is one step involved in uniaxial tensile deformation of non-crosslinked polyethylene: the process starts with tie molecule stretching, goes on with crystalline lamellae rotation and alignment (parallel to the direction of loading), fragmentation of the lamellae (strain softening, starting with crystal slip) and finally chain unfolding and alignment (strainhardening) occurs before rupture [14,154, 155]. For the crosslinked PE-UHMW, it is hypothesized that crosslinking limits lamellar alignment in plastic deformation process due to retardation in the orientation of the crystalline lamellae (crosslinking decreases chain mobility and mobility of the lamellae in the network) [154, 156]. When the stress is applied perpendicularly to the orientation direction, the strength of PE-UMW is reduced due to this deformation- induced structural anisotropy. The surface shear stresses are multi-directional in human hip and knee joints and generate a damage layer with structural anisotropy [80]. Wear of PE-UHMW acetabular cup occurs mostly on the surface, a result of adhesive and abrasive wear mechanism. Hence, orientation of crystal lamellae influences the wear behavior [80,156]. Orientations on molecular level have been investigated by Davey et al. [157]. They used a polarizing aperture for FTIR dichroic measurements in order to quantify the molecular orientation depending on the patients gait pattern. Orientation of the polymer chains in direction of the crystalline a-axis was observed in patients with a higher aspect ratio of the gait path (a more longitudinal path).

2.5 Mechanical properties of PE-UHMW at different length scale

PE-UHMW in hip endprosthesis is subjected to articulation and (cyclic) contact stress *in vivo*. Over time the accumulated damage results in formation of wear debris causing adverse body reactions. 3.5 % of the implants have to be retrieved because of catastrophic failures due to fracture of the component [45]. Hence, the failure of PE-UHMW in hip arthroplasty is linked to plasticity, fracture and fatigue behavior of the material itself [14]. Nevertheless, the interdependency of wear rate and conventional mechanical properties is not understood in PE-UHMW [80].

Macroscopic fracture is always based on the interaction of a crack tip with the material ahead of it. Microdeformation and micromechanics of the fracture determine the length scale, which is in the dimension as the morphology [158]. Micromechanical and macromechanical properties of PE-UHMW are discussed in 2.5.1 and 2.5.2, respectively.

2.5.1 Nano- and Micromechanical properties

Mechanical test methods for determining nano- and micromechanical properties of PE-UHMW are depth sensing indentation testing DSI (nano- and microindentation) and atomic force microscopy AFM (for very small indentation depths and nano-scratch experiments) [159].

The principles of depth sensing indentation testing are given in a review by Oliver and Pharr [160]. A hard indenter (typically made from diamond) is pressed into the surface of a sufficient thick sample of the material. The load and displacement is recorded during indentation (see Figure 19). Loading is assumed to involve elastic and plastic deformation, whereas during unloading only elastic displacement recovers [160]. In viscoelastic materials, which show time-dependent relaxation processes, a holding period at maximum load is required in order to account for these processes [159]. The load-displacement curve is used to calculate hardness and indentation modulus.



Figure 19: Principles of depth sensing indentation testing: load – displacement curve (left) and schematic illustration of the unloading process (right), both adapted from [160]; S ... contact stiffness, $h_f \dots$ final depth, $h_{max} \dots$ maximum displacement, $h_c \dots$ difference between maximum displacement and amount of sink-in;

Hardness H_{IT} is calculated according to [160]:

$$H_{\rm IT} = \frac{F_{\rm max}}{A} \tag{15}$$

with F_{max} being the load at maximal displacement and A the projected area under the indenter. The elastic nature of the unloading curve is used to calculate the effective elastic modulus E_{eff} by using the contact stiffness S:

$$E_{eff} = \frac{\sqrt{\pi S}}{2\beta\sqrt{A}} \tag{16}$$

The elastic modulus determined by indentation testing E_{IT} is calculated from:

$$\frac{1}{E_{eff}} = \frac{(1 - v^2)}{E_{IT}} + \frac{(1 - v_i^2)}{E_i}$$
(17)

where E_{IT} and the Poisson's ratio v are properties of the sample and E_i and v_i the according properties of the indenter material. Formula (15) and (16) involve the projected area under the indenter which changes during the testing and is determined by the actual geometry of the indenter. The area function $A = F(h_c)$ (see Figure 19, right) has to be calibrated [160]. Another approach is to measure the lengths of the residual imprint by SEM or AFM [159].

DSI testing is a quasi-non-destructive testing method which requires small sample volumes only. Nanoindentation uses maximal indentation depths up to 200 nm, above 200 nm and below maximum force of 2 N microindentation measurements are conducted [161]. Due to the deformation below the indenter, a sufficient sample thickness and spacing between the intents (and material borders) is required. Hence, mechanically properties can be evaluated locally resolved in dependence of the indentation depth.

The indentation technique is used for determining properties of PE-UHMW like hardness and indentation modulus. In most cases surfaces modified PE-UHMW is investigated [162-164]. Investigations employing DSI testing for evaluation of effects of *in vivo* use, crosslinking, and processing are rare.

Wernlé et al. [165] determined the relationship between oxidation level and micromechanical properties of shelf aged and retrieved knee components. Both bearings exhibited a positive linear correlation between oxidation and hardness as well as modulus.

Gilbert et al. [122,166] compared micromechanical properties of GUR 1020, high crystalline PE-UHMW modification (HylamerTM, not very successful *in vivo* [54]) and crosslinked PE-UHMW (MarathonTM; 50 kGy, remelting and annealing, see Figure 12). HylamerTM was shown to have the highest modulus and microhardness of the three, with GUR next and Marathon with the lowest values. Unfortunately no data on the polymer morphology are provided.

Zhou et al. [167] tried to relate the nano-mechanical properties of conventional and crosslinked (100 kGY, remelted) PE-UHMW to the wear behavior. Both material states showed similar mechanical behavior at nano-scale and whereas the micro-scale wear behavior was different. These results demonstrate the necessity of further length-scale dependent correlations of PE-UHMW on component level [167].

Park et al. [168] demonstrate that the indentation modulus of ram extruded GUR 1020 is higher than in the same material crosslinked by electron beam and peroxides. They also show a higher indentation modulus in GUR 1020 ram extruded compared with compression molded (on laboratory scale). Unfortunately, again no data on the polymer morphology are provided.

Flores et al. [169] showed that hardness value of PE-UHMW increases with annealing time at 130 °C as a consequence of higher degree of crystallinity.

Nano-scratch experiments are used as single-asperity wear experiments. An AFM tip is plowed across the surface and the piling up, fibrillation of the material, and the generation of particles is investigated [159]. The strain softening described by Wang et al. [80] is confirmed by nano-scratch experiments [170]. A study by Wong [171] suggests that intersecting scratches affect the wear rate and this is the major cause for wear-debris generation in PE-UHMW joint replacement.

2.5.2 Macromechanical properties

The mechanical behavior of bulk PE-UHMW plays an important role in long-term success of the endoprosthesis. Specific mechanical properties of PE-UHMW (non-crosslinked or crosslinked) have to be determined according to ASTM F 648-04 [63] and ASTM F 2565-06 [65] by the following methods:

- Quasi-static tensile test (ASTM D 638 [172], ISO 527 [173]) dogbone specimen
- Izod impact test (ASTM F 648 [63]) or Charpy impact test (ISO 11542 [1,71]) double notched specimen have to be employed. Standard specimen (e.g. according to ASTM D 256-05 [174]) do not to break when tested with a 50 J pendulum due to the very high toughness of PE-UHMW.
- Quasi-static compression test (ASTM D 1621 [175])
- Fatigue crack propagation (ASTM E 647 [176]) usually compact tension (CT) specimen
- Small punch test (ASTM F 2183-02 [177])
- Some other methods can be applied by industry [60,64,178]:
- Deflection temperature (ASTM D 648 [179])
- Flexural modulus (ASTM D 790 [180])
- J-integral test (ASTM E 813 [181]) usually compact tension or three point bending specimen
- Creep test (ASTM 2990 [182])

This list of mechanical tests does not include all tests that may be required to explore the properties of a new PE-UHMW modification. Furthermore, regulatory agencies, such as the Food and Drug Administration (FDA), may ask for additional tests [178].

Specimen geometries like dogbone, CT or three point bending do not allow testing of hip implant PE-UHMW components. The small punch test, a miniaturized bi-axial disc bend test, allows mechanical characterization on component level [23,184]. During this test the load-displacement curve is recorded and peak load, ultimate load, ultimate displacement, and work to failure are calculated [177]. Although work to failure is a characteristic toughness value, the fracture mechanical behavior of the material cannot be determined by this method. An overview about application of the small punch test in investigation of PE-UHMW for orthopedic application is given in [183]. Only aspects of mechanical degradation during *in vivo* use are discussed hereafter.

A study of mechanical behavior of retrieved PE-UHMW components after more than ten years *in vivo* was published by Edidin et al.[23]. The explants were made from a historical PE-UHMW type similar to GUR 1020 containing calcium stearate. All explants showed evidence of mild to moderate mechanical degradation evaluated by small punch test. No information on structural parameters of PE-UHMW is given. The work to failure decreases with increasing body weight of the patients. The findings suggest that the change in mechanical behavior is influenced by magnitude load during *in vivo* use and sensitivity to cyclic loading. Small punch testing of retrieved hip implants (*in vivo* time > 10 years) showed significant higher mechanical degradation in the unworn region compared with the unworn region. The study was not designed to allow conclusions if this novel and surprising findings are attributed the fact that the degraded material was already removed in the worn regions [183].

The quasi-static tensile properties are well investigated in the field of PE-UHMW for orthopedic application. The standard method is employed for investigations on powder type, processing conditions, crosslinking procedures, thermal treatment and sterilization protocols [14]. For example four studies which investigated material states similar to those tested in this Thesis (see 3.1):

Kurtz et al. [185] investigated the tensile properties of virgin, ram extruded GUR 1050 and the same material gamma sterilized in nitrogen (30 kGy), radiation crosslinked (100 kGy) and remelted, and radiation crosslinked (100 kGy) and annealed. They found that the degree of crystallinity and the radiation dose are key predictors in modulus, uniaxial yielding, plastic flow, and failure. True ultimate strain and stress decrease linearly with increasing irradiation dose. The yield strength increases with increasing degree of crystallinity.

Deng et al. [121] investigated virgin GUR 1050 and gamma-irradiated material (25 kGy, under nitrogen, vacuum, air and acetylene). Upon real time aging up to 5.5 years the degree of crystallinity increased and the tensile modulus increased whereas the stress and elongation at break decreased.

Gomoll et al. [186] investigated virgin ram extruded GUR 1050 irradiated under nitrogen at doses of 25, 50, 100, and 200 kGy. All material states were remelted (175 °C), and annealed (125 °C). The degree of crystallinity was lower (3 - 5%) in the irradiated material states. The tensile yield stress did not differ between the material states, true strain at break was reduced with increasing irradiation does, and the true stress at break was significantly reduced only at high irradiation doses (100 and 200 kGy)

Morrison et al. [84] investigated the effect of gamma-irradiation with single dose and three sequences (both material states total irradiation dos 90 kGy) and annealing compared to single dose and remelting on compression molded GUR 1020. Sequential irradiation had not influence on yield strength, ultimate tensile strength and elongation at break compared with single dose irradiation. All crosslinked material states exhibited significant lower ultimate tensile strength and elongation at break. In irradiated and remelted PE-UHMW the ultimate tensile strength was reduced compared with irradiated and annealed material states.

The fracture behavior of PE-UHMW is investigated not only by tensile tests and other mechanical tests but also by test methods based on fracture mechanical concepts. Fracture mechanics testing methods allow determination of the fracture toughness in polymers. The

methods are based on testing of specimens containing a crack with known geometry and the evaluation of crack-growth as a function of loading parameters.

Two approaches are applicable in general [161]: linear elastic fracture mechanics (the concepts involving stress intensity factor K and energy release rate G) and elastic-plastic fracture mechanics (the concepts involving the crack tip opening displacement δ , the J-integral concept, and the essential work of fracture concept).

In PE-UHMW the application of the linear elastic fracture mechanics (LEFM) concept is limited to cyclic loading (fatigue crack propagation) conditions, due the very high toughness of PE-UHMW [14,187]. The characteristic parameter of LEFM is the stress intensity factor K_I (fracture toughness under plane strain conditions and crack-opening mode I), based on [161]:

$$K = \sigma \sqrt{\pi a} f(a/W) \tag{18}$$

with σ the stress, a crack length and f(a/W) a geometric function reflecting specimen and crack geometry. The concept implies elastic material behavior ahead of the crack tip. If K_I becomes higher than a critical value K_{IC}, fracture occurs.

Gencur et al. [16] evaluated the fracture toughness indirectly for fracture surface of specimen broken under quasi-static tensile loading. Virgin, ram extruded GUR 1050 and the same material gamma sterilized in nitrogen (30 kGy), radiation crosslinked (100 kGy) and remelted, and radiation crosslinked (100 kGy) and annealed were tested (see also [185]) and the critical flaw size a was evaluated from the fracture surface by SEM. The fracture toughness Kc was estimated using $K_c = 1.13 \sigma a^{1/2}$ (fully embedded flaw) and $K_c = 1.27 \sigma a^{1/2}$ (surface flaw). Fracture toughness in terms of K_c was higher in the virgin and radiation sterilized than in both the highly crosslinked material states. Though there was a significant difference in percent crystallinity between the two crosslinked material states, no significant difference was found in K_c . No clear influence of percent crystallinity on K_c was evaluated from all material states.

If LEFM is not applicable due to elastic-plastic material behavior ahead of the crack tip under the loading conditions, the J-integral concept is used for investigation of PE-UHMW fracture toughness [14]. The J-integral characterizes the interaction of a crack tip and the polymer by a path-independent contour integral which encloses the plastically deformed region ahead of the crack tip. Its path of integration R is in the elastic deformed region around the crack tip. It represents the energy needed to extend the crack [161]:

$$J = \int_{R} \left(w dy - T \frac{du}{dx} dR \right)$$
(19)

with w the strain energy density, x and y coordinate directions, T the traction vector and u the displacement vector. This integral can be solved by approximation [188]:

$$J = \frac{\eta U}{B_N (W - a_0)} \tag{20}$$

with η a geometrical factor, U the energy required to extend the crack, B_N specimen net thickness, W specimen width and a₀ the original crack length. Relevant standards are ASTM D 6068 [188], and ASTM E 1820 [189].

Physical crack initiation, the beginning of stable crack growth, is characterized by J_I (under plain strain conditions and crack-opening mode I) becoming higher than a critical value J_{IC} . If geometrical requirements for plain strain conditions at the crack tip are not met, i.e. plain stress conditions or combinations of both conditions, J_Q , conditional J_{IC} values, are reported [190,191]. These values are not independent from specimen geometry. The technical crack initiation value $J_{0,2}$ represents the J-integral value at crack extension of 0.2 mm [192] and is

used as characteristic fracture toughness value. When the J-integral value is plotted as a function from crack extension, J-R curves are generated. The slope and shape of these fracture resistance curves give information on the toughness, i.e. the energy required for crack growth. J_{IC} was found to be 99.5 kJ/m² in ram extruded PE-UHM [190] which is a high value compared with other tough engineering plastics or e.g. PE-HD where J_{IC} is around 10 kJ/m² [193]. J_{O} is reduced due to gamma-sterilization in air by approximately 50 % and a less stable crack growth was observed [191]. The study by Gomoll et al. [186] already mentioned above, evaluated stable crack growth behavior. The resistance decreased with increasing irradiation dose. Cole et al. [194] investigated the (fatigue and) fracture behavior of different PE-UHMW types (1900H and GUR 1050, isostatic compression molded), irradiated at doses 0, 33, 66, and 100 kGy, subjected to pressurized hydrogen and annealed. The fracture toughness J_Q was 28 % higher in virgin 1900H than in virgin GUR 1050. At 33 kGy the J_Q of GUR 1050 was higher than in 1900H and virgin GUR 1050. No explanation of this finding is published. The conditional crack initiation value decreased with further increase in irradiation dose. The resistance against stable crack growth, indicated by lower slope in the J-R curve at higher crack extension values, depended on PE-UHMW type. Unfortunately, no data on structural parameters are given in this study. Varadarajan et al. [195] investigated J crack initiation toughness in ram extruded GUR 1050, gamma-sterilized (30 kGy under nitrogen), crosslinked and remelted (65 kGy, 150 °C), and crosslinked and annealed (65 kGy, 130 °C). J_Q is 22 % and 31 % lower in crosslinked and annealed and remelted PE-UHMW respectively than in gammasterilized material. Both crosslinked material states show similar resistance to crack initiation. Furthermore, it was found that the test performed in phosphate buffered saline at 37 °C resulted in reduced fracture toughness. The fracture behavior in terms of shape of the J-R curves was similar in all material states.

Another study by Varadarajan et al. [196] investigated the J fracture behavior of sequentially crosslinked and annealed compression molded GUR 1020 (M1), gamma-sterilized ram extruded GUR 1050 (M2), gamma-sterilized compression molded GUR 1020 (M3), as-received GUR 4150 (M4), and crosslinked and remelted GUR 1050 (100 kGy, 150 °C; M5). The J-R curves demonstrated a fracture resistance of M4 > M3 > M2 with small differences, and the crosslinked material showing lower resistance against crack growth with M1 being tougher than M5. Again, the fracture behavior in terms of shape of the J–R curves was similar in all material states and no structural data are given.

Mendel et al. [197] showed a tougher behavior (in terms of J-R curves) in crosslinked and annealed compression molded GUR 1050 (100 kGy, 130 °C) compared with as-irradiated material. Crosslinked and remelted PE-UHMW (100 kGy, 150 °C) exhibited reduced toughness compared with as-irradiated material. All irradiated material states showed lower resistance against crack growth than non-irradiated PE-UHMW. The lamellar thickness does not correlate with the fracture behavior. It seems more feasible to the authors that the rise in crystallinity caused the slight fracture resistance enhancement in crosslinked and annealed PE-UHMW.

Fatigue is the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. Structural damages lead to formation of microscopic cracks and their coalescence to a macroscopic crack that propagates in a stable manner until instability or complete fracture is reached. Fatigue life is defined as number of loading cycles needed to reach catastrophic failure [198]. The loading of an implant during movement of the patient is cyclic in nature. Hence, the resistance to fatigue fracture is an important issue in prosthesis design and clinical considerations.

Fatigue fracture behavior can be assessed on the basis of LEFM concept. The crack extension per loading cycle is depicted as a function of ΔK , the stress intensity factor range during cyclic loading. The resulting curve shows three regimes [14]: the threshold regime, where no substantial the crack growth is measurable (characterized by ΔK_{th}), the Paris regime where

stable crack growth occurs (characterized by Paris lower law relationship) and finally, the fast fracture regime (onset characterized by K_c).

In PE-UHMW fatigue crack propagation (FCP) is affected by irradiation. The main reason for the reduced FCP resistance in irradiated PE-UHMW is attributed to the reduced capacity for plastic deformation due to crosslinks. Increasing irradiation dose results in reduced ΔK_{th} and reduced resistance to stable crack growth [18,104,187,193, 196, 198]. Remelting of crosslinked PE-UHMW reduces the resistance against FCP [104] more than annealing does [196,199] and no thermal treatment [200]. A positive effect of higher degree of crystallinity of the FCP was shown [196]. Simis et al. [201] found that ΔK_{th} scales better with lamellar thickness than with the degree of crystallinity and that high pressure crystallization enhances fracture resistance.

 ΔK_{th} was found to be similar in compression molded GUR 1050 and GUR 1050 containing 0.3 wt% vitamin E. The addition of vitamin E reduced the decrease of ΔK_{th} by gamma-irradiation [202]. E. Oral et al. [200] showed doping crosslinked UHMWPE with vitamin E could increase fatigue resistance (due to avoiding remelting step).

Oral et al. [203] investigated the effects of high pressure crystallization (180 °C, 310 MPa) and different concentrations of vitamin E on structure and mechanical properties of compression molded GUR 1050. Inter alia they found that high pressure crystallization improved the fatigue strength, which was additionally significantly better in samples containing vitamin E. The fracture behavior is different, high pressure crystallized material shows cavitations, whereas non-high pressure crystallized material states do not.

Under cyclic loading conditions static mode crack propagation (slow crack growth) occurs. In PE-UHMW the static mode dominates and hence, cracks can grow without significant cyclic loading [204].

Generally, structure properties correlations enable optimization of polymeric material for specific applications. In the field of PE-UHMW research either focus on mechanical properties e.g. [190] (or wear) or structural parameters e.g. [70,106,116,119]. If a study investigates both, structural parameters and mechanical properties, the correlations are often limited to the degree of crystallinity (see 2.5.2).

Another issue in comparing literature data is that for reasons of commercial sensitivity many of the crosslinking and thermal treatment procedures applied to material under investigation are not described properly [70]. Furthermore, the results are sometimes contrary, indicating the complexity of the task.

3 Materials and Methods

3.1 Material states

The PE-UHMW material states are chosen to investigate the influence of molar mass, additivation with vitamin E, consolidation, machining of hip liners, irradiation-sterilization, crosslinking followed by a thermal treatment (remelting and annealing), and *in vivo* use (exemplarily). The following material states are investigated in order to evaluated

- the influence of consolidation:
 - GUR 1050, medical grade, ram extruded rod (Orthoplastics Limited, Lancashire, UK; material state shortcut: RER)
 - GUR 1050, medical grade, compression molded sheet (Orthoplastics Limited, Lancashire, UK; material state shortcut: CMS)
- the influence of molar mass and additivation by Vitamin E:
 - GUR 1050, medical grade, compression molded sheet (Orthoplastics Limited, Lancashire, UK; material state shortcut: GUR 1050)
 - GUR 1020, medical grade, compression molded sheet (Orthoplastics Limited, Lancashire, UK; material state shortcut: GUR 1020)
 - GUR 1020, medical grade containing 0.1 wt% Vitamin E, compression molded sheet (Orthoplastics Limited, Lancashire, UK; material state shortcut: GUR 1020VitE)
- manufacturing:
 - virgin acteabular components turned from GUR 1050, medical grade, ram extruded, non-sterilized (material state shortcut: 1050 ng)
 - virgin acteabular components turned from GUR 1020, medical grade, compression molded, non-sterilized (material state shortcut: 1020ng)
- gamma-sterilization:
 - virgin acteabular components turned from GUR 1050, medical grade, ram extruded, gamma-sterilized under inert atmosphere (material state shortcut: 1050g)
 - virgin acteabular components turned from GUR 1020, medical grade, compression molded, gamma-sterilized under inert atmosphere (material state shortcut: 1020g)
- crosslinking and thermal treatment
 - virgin, commercially available acteabular components made from Durasul® (Zimmer Inc., Warsaw, IN, USA; material state shortcut: Dsa)
 - virgin, commercially available acteabular components made from Longevity[™] (Zimmer Inc., Warsaw, IN, USA; material state shortcut: Lsa)
 - virgin, commercially available acteabular components made from X3TM (Stryker Howmedica Osteonics, Mahwah/Rutherford, NJ, USA; material state shortcut: X3sa)

All acetabular components (size 28) are investigated in as received material state. The components 1020ng, 1050ng, 1020g, and 1050g have been produced by a big manufacturer of orthopedic devices for investigations within the scope of this Thesis only. These virgin acteabular components have never been intended to be used *in vivo*.

Irradiation sterilized PE-UHMM hip implants have been implanted since the late 1960s. Nowadays, Durasul[®] and $X3^{TM}$ acetabular components are frequently implanted in Austria. Therefore, it has been possible to investigate explants made from three material states:

- Irradiation sterilized PE-UHMM explant (Alloclassic® design, former Sulzer Orthopaedics, Switzerland, today Zimmer Inc., Warsaw, IN, USA; material state shortcut: MAS)
- Durasul (Alloclassic® design, Zimmer Inc., Warsaw, IN, USA; material state shortcut: GAN)

• X3(Stryker, Howmedica Osteonics, Mahwah/Rutherford, NJ, USA; material state shortcut: FIN)

Table 6 summarizes the material states.

Table 6: Material states – summary of the applied manufacturing step during life cycle; a) molar mass calculated from viscosity data provided by Ortoplastics according to DIN EN ISO 1628-3 using Mark-Houwink equation [24], b) molar mass according to [28], c) GUR 1020 additivated by 0.1 %wt Vitamin E

material	(initial) molar mass (10 ⁶ g/mol)	consolidation	crosslinking and thermal treatment	sterilization	time in vivo	acronym
GUR 1050	5.49 ^{(a}	compression molding	-	-	-	CMS
GUR 1050	5.49 ^{(a}	ram extrusion	-	-	-	RER
GUR 1020	3.82 ^{(a}	compression molding	-	-	-	GUR 1020
GUR 1020 ^{(c}	3.5 ^{(a}	compression molding	-	-	-	GUR 1020VitE
GUR 1050	5.68 ^{(a}	compression molding	-	-	-	GUR 1050
GUR 1020	3.5 ^{(b}	compression molding	-	-	-	1020ng
GUR 1050	5.5 ^{(b}	ram extrusion	-	-	-	1050ng
GUR 1020	3.5 ^{(b}	compression molding	-	gamma (N ₂)	-	1020g
GUR 1050	5.5 ^{(b}	ram extrusion	-	gamma (N ₂)	-	1050g
Durasul®	5.5 ^{(b}	compression molding	95 kGy, 120 °C; remelting (150 °C 2h)	gas (EtO)	-	Dsa
Longevity TM	5.5 ^{(b}	compression molding	100 kGy, 40 °C; remelting (150 °C 6h)	gas (EtO)	-	Lsa
X3 TM	3.5 ^{(b}	compression molding	90 kGy (3× 30 kGy); 3 × annealing (135 °C)	gas (plasma)	-	X3sa
Durasul®	5.5 ^{(b}	compression molding	95 kGy, 120 °C; remelting (150 °C 2h)	gas (EtO)	1 year	GAN
X3 TM	3.5 ^{(b}	compression molding	90 kGy (3× 30 kGy), 3 × annealing (135 °C)	gas (plasma)	unknown	FIN
irradiated GUR	unknown	unknown	-	irradiation	unknown	MAS

3.2 Sample preparation

One aim of this Thesis is to figure out local inhomogeneities resulting from the manufacturing processes and *in vivo* use. Two areas in the implants were investigated: the rim area and the center area (see Figure 20, middle and right, part number 4). Structural parameters and the micro-mechanical properties are investigated as a function from distance from inner and outer surface. Depth profiles of characteristic values are generated.



Figure 20: Schematic diagram of a hip liner: left - hip implant (as received); middle - split hip implant (1, 3, 5 were used for preliminary tests, other investigations not published in this Thesis, and kept for remeasurements, 2 for arc-shaped specimens, 4 see right); right – sample preparation for investigations on local inhomogeneities (part 4, split, explanations of numbers 4a – 4d see text below);

In order to generate these depth profiles small pieces are cut from the rim and center part (see Figure 20, right, 4a - 4d). The smaller pieces were prepared regarding the need of the analytical methods (see 3.3 and 3.4):

- For Fourier transformed infrared spectroscopy (FTIR) slices of app. 180 μm thickness were microtomed parallel to the inner surface from part 4b (see Figure 20), and parallel to the outer surface from part 4c (see Figure 20). The material which was clamped is discarded due to heavy mechanical deformation. The thickness of the microtomed slices was measured with a micrometer gauge.
- The slices investigated by FTIR were cut into two samples and analysed by differential scanning calorimetry experiments (DSC).
- For depth sensing indentation measurements (DSI), part 4d was embedded in epoxy resin. The embedded sample was grinded (water cooled) and polished (final polishing paste contained 1 µm diamond particles). The final sample thickness was in the range of a few mm. The prepared surface was perpendicular to inner and outer surface. The depth profiles from inner surface and outer surface towards the center of the component were measured on the same sample.
- Part 4a (see Figure 20, right) was kept as a reference in case that some of the measurements have to be repeated.

The specimens used for characterization of the fracture toughness were machined from part 2 (see Figure 21, left) and grinded to final geometry. Specimen shape is based on arc-shaped specimen geometry proposed by ASTM E 399 - 90 [205] and successfully applied to polymers by [206-208].



Figure 21: Position of the arc shaped specimen (grey) within part 2 (see Figure 20) – left; specimen dimensions (in mm) – right; W ... specimen width, B ... specimen thickness, R ... radius of the arc shaped specimen, a_0 ... original crack size, a_s ... size of the side groves; values are given in mm;

The specimen size (see Figure 21, right) is chosen with regard to hip implant geometries: EN 12563:1998 gives a minimum thickness of 5 mm for metal backed PE-UHMW hip liners. Hence, maximum specimen width W can be 5 mm for specimen machined directly from the PE-UHMW liner. Specimen thickness B is a crucial factor in fracture toughness testing on the basis of fracture mechanical principles. The plain strain condition ahead of the crack tip (and hence, the independence of the evaluated characteristic values from specimen thickness, W/B was set 1. Currently, the most frequently implanted liner size has an inner diameter of 28 mm [55] and an inner radius of 14 mm. By addition of W, the radius of arc-shaped specimen is R = 19 mm. The thickness of the ligament (W-a₀) should be high to avoid excessive plasticity. In order to generate mechanically harsh conditions at the crack tip, the initial crack length a₀ is set a₀/W = 0.1, a₀=0.5 mm. Side groves a_s are used to promote straight crack front during testing, a_s/B = 0.005, a_s = 0.25 mm.

In order to evaluated the dependency of the fracture toughness from the specimen thickness B single edge notched bend (SENB) specimen with B = 20, 10, and 5 mm made from ram extruded GUR 1050 were tested (see 3.4.2). SENB specimens behave mechanically similar to arc-shaped bending specimen [206]. The geometrical ratios (W/B = 1, $a_0/W = 0.1$, and $a_s/B = 0.005$) were kept constant. The number of specimen tested n was 5.

The sample preparation for FTIR and DSC measurements of compression molded sheet (CMS, thickness 50 mm) and ram extruded rod (RER, diameter 60 mm) is shown schematically in Figure 22: First a cubiod was cut from both material states (along the red lines). These samples were cut in cubes with side length 10 mm (along the green lines). Approximately 180 μ m thick slices were microtomed from the outer surface of each cube inwards.



Figure 22: Sample preparation from compression molded sheet CMS and ram extruded rod RER (both GUR 1050; lot form May, 2007

The data from all test methods was statistically treated with origin 6.0 software. A one way ANOVA test was performed with a significance level of 0.95 (p < 0.5, one-way ANOVA).

3.3 Applied methods for determination of structural parameters

3.3.1 Fourier transformed infrared spectroscopy – FTIR

The principles of FTIR analysis can be found in [210]. The FTIR analytics of polymers is different compared to the analytics of a single chemical compound (analyte) dispersed in a matrix. First, in polymers the analyte and the matrix are the same (except if FTIR analysis is performed in solution of the polymer). Second, the analyte is not a single compound but chemically similar substances e.g. the oxidation of polyethylene leads to keton groups, this keton group is statistically formed anywhere on the polymer backbone, and this leads to ketons with C-C - chains of different length bound to the CO – double bond. This results in a broadening of the corresponding peaks [211].

The FTIR analyses were performed with a Tensor 27 (Brucker Optics, Ettlingen, Germany) on mictrotomed PE-UHMW slices with app. 180 μ m thickness (see 3.2). The measurements were recorded in transmission with 16 scans per spectrum and a resolution of 2 cm⁻¹. The resulting spectra were manipulated with OPUS 6.0 software.

The oxidation index OI was calculated for evaluation of the oxidative degradation of the samples according to ASTM F 2102 [212]:

$$OI = \frac{A_{1650-1850cm^{-1}}}{A_{1330-1396cm^{-1}}}$$
(21)

where $A_{1650 - 1850 \text{ cm}-1}$ is the area of the peak centered around 1720 cm⁻¹ (carbonyl group), and $A_{1330 - 1396 \text{ cm}-1}$ is the area of a reference peak. The OI is a summary parameter which gives the amount of all carbonyl groups in the sample (semi-quantitatively).

Furthermore, the amount of keton - and ester group and their ratio to each other gives information on the oxidation mechanism e.g. thermo-oxidative [116] or mechano-oxidative [119], and biomolecules diffused into the implants *in vivo* [106] (see 2.3 and 2.4.1). For a more detailed investigation of these carbonyl species, the spectra were normalized [111,113]: the spectra were set to zero at 2100 cm⁻¹ and the height of the peak centered around 2020 cm⁻¹ was set 0.5 a.u. (corresponding to a film thickness of app. 100 μ m). These normalized spectra can be depicted as depth profiles (FTIR mapping). Unfortunately, ASTM F 2102 [212] does not specify the quality of the FTIR spectra (e.g. in terms of peak height) which enables calculation of OI. Hence, at very low concentrations of carbonyl- groups maybe rather the base line is integrated than a peak. The reported values scatter [81], and for meaningful interpretation the normalized spectra should be used in addition.

Additionally, the trans vinylene index TVI was calculated according to ASTM F 2381 [213]:

$$TVI = \frac{A_{950-980\,cm^{-1}}}{A_{1330-1396\,cm^{-1}}}$$
(22)

where $A_{950-980 \text{ cm-1}}$ is the area of the peak centered around 965 cm⁻¹ (trans vinylene group), and $A_{1330-1396 \text{ cm-1}}$ is the area of the reference peak. The trans vinylene group is formed during irradiation of the PE-UHMW. The TVI gives a semi- quantitative measure for the total irradiation dose the sample was subjected to. It is used as internal dosimeter in order to establish dose-depth profiles. Again, especially at low radiation doses the reported TVI values scatter [76].

The terminal vinyl group is formed during synthesis of PE-UHMW or during high temperature melting [74,114]. The consumption of terminal vinyl groups during irradiation indicates Y-

crosslinking mechanism [113], see 2.4.1. The content is semi-quantified and denoted as terminal vinyl index TermVI:

$$TermVI = \frac{A_{909\,cm^{-1}}}{A_{1330-1396\,cm^{-1}}}$$
(23)

where $A_{909 \text{ cm-1}}$ is the area of the peak centered around 909 cm⁻¹ (terminal vinyl group), and $A_{1330-1396 \text{ cm-1}}$ is the area of the reference peak.

Degree of crystallinity X_{FTIR} (%) was calculated from FTIR data according to [214]:

$$X_{FTIR} = \left(\frac{\left(\frac{A_{1896cm^{-1}}}{A_{1305cm^{-1}}}\right)}{\left(\frac{A_{1896cm^{-1}}}{A_{1305cm^{-1}}}\right) + 0,25}\right) \times 100$$
(24)

In this empirical formula $A_{1896cm-1}$ is the area of the peak centered around 1896 cm⁻¹ (crystalline band) and $A_{1305 cm-1}$ is the area of the peak centered around 1305 cm⁻¹ (amorphous band).

Lambert-Beer's law [210] was used for direct quantification of the ester group in explants:

$$\Phi_{ex} = \Phi_{in} \times e^{-\kappa_n cd} \tag{25}$$

with Φ the intensity of the IR beam before passing the sample (in) and after passing the sample (ex), κ_n the molar extinction coefficient, d sample thickness, and c concentration of the analyzed group. Lacoste et al. [215] reported κ_n to be 590 l/mol cm for the ester group. The peaks of the vinylene - and vinyl- unsaturations are in the region where the spectra exhibit a wavy baseline due to Fourier rippling. Hence, direct quantification involving the peak height instead of the peak area is not favorable.

All indices were depicted as functions of the distance from implant surface (depth profiles) [212].

3.3.2 Differential scanning calorimetry – DSC

The principles of differential scanning calorimetry (DSC) are explained in [216]. The experiments were performed on a Q2000 DSC (TA Instruments, New Castle, DE, USA). The microtomed slices, investigated by FTIR previously, were cut into two samples per slice with a mass of app. 1 - 2 mg each. The mass was determined by an analytical balance with a resolution of \pm 0.01 mg. The DSC samples were encapsulated in standard pans made from aluminum (the mass of the pan and the lid were considered in the evaluation of the DSC results automatically by the TA software).

The samples were then subjected to a temperature program: they were heated with 10 °C/min from 0 °C to 220 °C, equilibrated at 220 °C for 5 min, cooled with 10 °C/min to 0 °C, equilibrated at 0 °C for 5 min, and again heated with 10 °C/min to 200 °C. The experiment results in a DSC curve which gives the difference in heat flow between the sample and a reference pan (empty aluminum pan) as a function of temperature (or time).

Generally, the first heating run reflects the chemical and physical structure of the polymer including its thermal and mechanical history, e.g. physical aging, annealing effects, changes in the crystalline phase due to mechanical loading. The second heating run reflects the chemical

structure of the polymer only (due to the similar crystallization conditions in the cooling run), e.g. oxidative degradation, crosslinking.

From the DSC curve characteristic temperatures were determined: the melting temperature from the first T_{m1} and the second heating run T_{m2} , the onset temperature of crystallization $T_{c,onset}$ (the temperature in the DSC cooling run, where the extothermal crystallization peak starts to differ from the baseline), and the temperature at the maximum of the crystallization peak T_c . The area beyond the endothermal melting peaks $\Delta H_{endotherm}$ (first and second heating run) was used to calculate the degree of crystallinity X_{DSC} (%) [5]:

$$X_{DSC} = \frac{\Delta H_{endotherm}}{\Delta H_f} \times 100$$
(26)

For PE-UHMW ΔH_f , the area of the endothermal peak of a theoretically 100 % crystalline PE-UHMW, is 291 J/g [5].

The structural parameters at nanometer level were calculated from DSC curves. The maximum in the melting peak gives information on the average lamellar thickness l_c . It can be calculated from the melting temperature T_m according to Thomson-Gibbs equation [217]:

$$l_{c} = \frac{2\sigma_{e}T_{m}^{0}}{\Delta H_{f}(T_{m}^{0} - T_{m})\rho_{c}}$$
(27)

 $T_m^0 = 418.15$ K is the equilibrium melting temperature for PE-UHMW [218], $\rho_c = 0.99$ g/cm³ the density of the crystalline phase [219], $\sigma_e = 0.09$ J/m² [217].

The data from DSC measurements are related with polymer mass. In order to obtain length parameters (nm) the data has to be related to the volume. With the crystalline mass fraction $x_m = X_{DSC}/100$ and $\rho_a = 0.85$ g/cm³ [219] the density of the polymer is calculated according to:

$$\rho = \frac{1}{\left(\left(\frac{x_m}{\rho_c}\right) + \left(\frac{1 - x_m}{\rho_a}\right)\right)}$$
(28)

and the crystalline volume fraction x_v is calculated:

$$x_{v} = \left(\frac{\rho}{\rho_{c}}\right) x_{m} \tag{29}$$

With these parameters the long period l_p and the average thickness of the amorphous phase l_a are calculated according to:

$$l_{p} = \frac{l_{c}}{x_{v}}$$
(30)
$$l_{a} = l_{p} - l_{c}$$
(31)

The structural parameters at nanometer scale determined by DSC experiments are depicted as a function from distance from implant surface (depth profiles).

The shape of the DSC endotherms gives a distribution of melting temperatures that can be converted to a distribution in lamellar thickness 1 [220]. The lamellar thickness distribution (LTD) can be calculated according to [147]:

$$\frac{1}{M} \times \frac{dM}{dl} = \frac{Heat \ flow}{Heat \ rate} \times \frac{\left(T_m^0 - T_m\right)^2 \rho_c}{2\sigma_e T_m^0} (32)$$

The probability of tie molecule formation given by equation (1) is calculated using the analytical solution for the integral [142]

$$\int_{0}^{\infty} r^{2} e^{-b^{2}r^{2}} dr = \frac{\sqrt{\pi}}{4b^{3}}$$
(33)

Now it is possible to write equation (1) in this way [221]

$$p = \frac{1}{3} \frac{\frac{\sqrt{\pi}}{4b^3} - \int_0^{l_T} r^2 e^{-b^2 r^2} dr}{\frac{\sqrt{\pi}}{4b^3}}$$
(34)

The Simpson rule is used to perform numerical integration of $\int_{0}^{l_{T}} r^{2}e^{-b^{2}r^{2}} dr$ with $l_{T} = 2l_{c} + l_{a}$ and

equations (2) and (5) using MatLab software.

3.4 Determination of micro- and macromechanical properties

3.4.1 Depth sensing indentation testing – DSI

The device used for the majority of tests was Nano Hardness Tester (CMS, Switzerland). A Berkovic indenter, a three sided pyramid, made from diamond was used. The samples were subjected to loading with 120 mN/min to a maximum depth of 5 μ m, followed by a holding period of 30 s to allow creep processes to occur and unloading with 120 mN/min (see scheme shown in Figure 18). After the measurements, the contact point (where the indenter touches the PE-UHMW surface) was evaluated from the load-displacement depth curve.

From the load-displacement curve, the micro-hardness and indentation modulus are calculated according to equation (15) and equation (17) respectively by Indentation 4.12 software. The Poisson's ratio of the UHMWPE it is 0.43 [168].

The test series have been established in order to measure H_{IT} and E_{IT} as a function of distance from implant surface (depth profile). The value for each distance was the mean value of five individual measurements. A resulting grid of measurement points is shown in Figure 23 exemplarily.



Figure 23: Embedded sample (left): AO - outer surface of the implant, IO – inner surface of the implant; measurement grid (right): regular spacing form the implant surface inwards shown exemplarily

Some measurements were conducted on a different Triboindenter® (Hysitron; see 4.2.3.1). A similar sample preparation and evaluation procedure was used to measure depth profiles of H_{IT} and E_{IT} , but the testing method was different: loading with 0.5 mN/s up to a maximum load of 10 mN, holding for 10 s, and unloading with 10 mN/s.

3.4.2 Fracture toughness testing on the basis of the J-Integral concept

3.4.2.1 Test method

The standard testing method for determining J-R curves of plastic material is described in ASTM D 6068-96 [188]. The influence of the specimen shape and specimen geometry on the fracture behavior of PE-UHMW was evaluated previous to the testing of hip implants (the same material state, GUR 1050, ram extruded rod, was used). Tests concerning the dependency of fracture toughness on specimen thickness were performed on single edge notched three point bending (SENB) specimens. Three different dimensions were tested: B = W = 5 mm, 10 mm and 20 mm (geometry shortcut: 5×5 , 10×10 and 20×20 respectively). Geometric ratios were kept constant (see 3.2). The results for the SENB specimen 5×5 were compared to the results of the arc shaped specimens in order to evaluate the influence of specimen shape on the fracture toughness.

All specimens were tested in three-point bending under quasi-static conditions at room temperature with a servo-hydraulic testing machine Z050 (Zwick Gmbh&Co.KG, Ulm, Germany). The specimen span S was 4W. The crack growth was monitored by means of an optical microscope equipped with a camera (Axio Cam HRc5, Carl Zeiss GmbH, Oberkochen, Germany). The outer fiber strain rate was set 0.135 min⁻¹ in order to allow a sufficient number of photos to be taken during the tests (resulting in test velocities v: v(W=5) = 2, v(W=10) = 4, and v(W=20) = 8 mm/min). The test configuration is shown in Figure 24, left. The load displacement curve was recorded. Simultaneously, the crack tip region was photographed every 2 s.

The physical crack size a_p and the total crack tip opening δ_{total} (further discussion see 3.4.2.2) was evaluated from these photos by using AxioVisio 4.7 software (see Figure 24, right). The physical crack extension Δa was the calculated:

$$\Delta a = a_p - a_0 \tag{35}$$

where a_0 is the original crack size. Then, Δa was attributed to a designated point in the load-displacement curve.



Figure 24: left – testing configuration: the traveling optical microscope equipped with a camera is installed in front of the specimen (the three point bending setting); right – evaluation of the physical crack size a_p and the total crack tip opening δ_{total} from the photos taken during the experiment

After the experiments, the specimen were cooled in liquid nitrogen and broken. The fracture surface allowed evaluation of the actual original crack size a_0 and the actual size of the side groves a_s . These lengths were measured by means of optical microscopy (Zeiss Stemi 2000-C microscope equipped with Zeiss AxioCam; the photos were evaluated again with AxioVisio 4.7 software). Furthermore, the fracture micro-mechanism was evaluated from the fracture surface by means of scanning electron microscopy (SEM).

The J-integral values were calculated according to equation (20) and the J-R curves were constructed by depicting J-integral values as a function of Δa . In equation (20) the following values were used: $\eta = 2$ for SENB [188] and for arc-shaped specimen [206] and B_N the specimen net thickness (for the side grooved specimens $B_N = B - a_s$). The energy required to extend the crack U was determined by subtracting the indentation energy U_i from the total energy U_T (area under the load-displacement curve) [188]:

$$U = U_T - U_i \tag{36}$$

The results of the method, using a traveling optical microscope, were compared to traditional multiple specimen technique according to ASTM D 6068 for the 5×5 specimen geometry.

3.4.2.2 Influence of testing technique, specimen shape, and geometry on the fracture toughness of PE-UHMW

Figure 25 shows a representative J-R curve of SENB 5×5 specimen calculated from monitoring the crack growth with a traveling optical microscope (single specimen test) and a J-R curve calculated from multiple specimen technique. The resulting curves are very similar, with the J-values for the multiple specimen method being slightly higher. This results from unloading the specimens where they bend back a little: the material in front of the crack tip is highly stretched in PE-UHMW (see 4.1.6). Upon unloading the material deforms back and the resulting crack extension measured from the fracture surface is smaller than the crack extension measured from the photo. Hence, the corresponding J values are slightly higher (approximately 0.01 - 0.05 mm) for the multiple specimen technique. With both methods the crack front is straight during testing due to the side groves.



Figure 25: Representative J-R curve from optical evaluation of crack-growth and from multi-specimen technique; J-R curve fitted by power law regression line $J = C_1 \Delta a^{C_2}$ with C_1 and C_2 being fitting parameters [188]

The physical crack initiation J_{IC} is a characteristic toughness value, which describes the onset of stable crack growth in a material (see 2.5.2.). It is characterized by a change of the slope in the J-R curve and can be evaluated by the intersection of the blunting line with the J-R curve [161], a simultaneous change in crack tip opening and crack extension as a function of displacement [195], or the J integral value of the crack extension corresponding to the stretch zone width evaluated from the fracture surface [161].

The J-R curves do not obviously show a point where the slope of the curve changes (Figure 25). Similar shape of J-R curves is reported for PE-UHMW [191,195].

Normally the blunting line is calculated by using the tensile yield strength σ_y [161]. In the field of PE-UHMW the blunting line is calculated using the ultimate tensile strength σ_M [190]. The tensile properties of GUR 1050 were determined using standardized specimen (type 5B according to EN ISO 527-2:1996 [173]). The tensile strain rate was the same as the strain rate in the bending tests (n = 7 specimens were tested). The resulting tensile yield strength σ_y is 18.2 MPa and the ultimate tensile strength σ_M is 28.1 MPa. The values are low because of the slow testing velocity. No intersection point between the blunting lines and the J-R curves is obtained (Figure 25).

The original crack length a_0 is very short. Hence the crack tip opening is very short too and it cannot be evaluated from the photos especially at the beginning of the measurements. In order to get a measure for the deformation of the crack tip the total crack tip opening δ_{total} was evaluated (see Figure 24). During blunting δ_{total} increases without significant crack extension Δa . At the onset of stable crack growth Δa increases in relation to a decrease in δ_{total} (slope of the δ versus displacement curve becomes lower [195]). The curves of δ_{total} and Δa as a function from displacement measured with this test method (see Figure 26) do not allow evaluation of the onset of stable crack growth.



Figure 26: Representative curves of total crack tip opening δ_{total} and crack extension Δa as a function from displacement in GUR 1050

The fracture surface has been evaluated by means of confocal scanning microscopy and SEM. No stretch zone is observed (Figure 27).



Figure 27: Evaluation of the fracture surface – results from confocal scanning microscopy (Axio CSM 700, Carl Zeiss Microimaging GmbH, Oberkochen, Germany)

These data indicates that the physical crack initiation J_{IC} cannot be evaluated under the employed testing conditions. Therefore, the crack initiation is evaluated in approximation by the technical crack initiation value $J_{0.2}$. This value is defined as the J-integral value at 0.2 mm crack extension by ESIS TC 4 [192]. The derivative of the J-R curve at crack extension 0.2 mm - $dJ/d\Delta a|_{0.2}$ - gives a measure for stabile crack growth [222]. Hence, this characteristic value is used to compare stable crack growth behavior of the material states and correlated it to structural parameters

In Figure 28 a representative J-R curve derived from arc-shaped specimen is compared with a J-R curve derived from a SENB 5×5 specimen. The fracture toughness is not sensitive to the specimen shape. This result is in good agreement with literature. Investigations on arc shaped specimen revealed a mechanically similar behavior of SENB and arc shaped specimens [206].



Figure 28: Representative J-R curves - comparison of results from arc-shaped and SENB specimens; J-R curves fitted by power law regression lines $J = C_1 \Delta a^{C_2}$ with C₁ and C₂ being fitting parameters [188]

Figure 29 shows representative J-R curves recorded from SENB-specimens geometry (5×5 , 10×10 and 20×20). The curves differ in terms of slope and final crack length, indicating that they depend on specimen geometry: Smaller specimens result in steeper the J-R-curves. An increase in slope reflects a higher resistance to crack growth. This increase can be attributed to the smaller specimen thickness. Hence, there are no plain strain conditions at the crack tip.



Figure 29: Representative J-R curves of different specimen geometries: SENB - 20×20, 10×10, 5×5; J-R curves fitted by power law regression lines $J = C_1 \Delta a^{C_2}$ with C₁ and C₂ being fitting parameters [188]

These results are in good agreement with literature data too, regarding the dependence of fracture toughness values in PE-UHMW on specimen thickness [190,191].

The established method allows comparing the fracture toughness of PE-UHMW on component level in terms of J-R curves, technical crack initiation value $J_{0,2}$ and stable crack growth value $dJ/d\Delta a|_{0,2}$. It is not possible to gain characteristic values which are independent from specimen thickness. Nevertheless, the fracture behavior of PE-UHMW hip implants in the same condition as they are available for the surgeons can be compared.

4 Results and Discussion

In chapter 4.1 the results from all material states (mean values) are discussed. The dependencies of mechanical properties on structural parameters are evaluated.

Anisotropy, induced by consolidation, manufacturing, physico-chemical treatment and *in vivo* use is discussed in 4.2. Variations of structural parameters and micro-mechanical properties are investigated as a function of distance from surfaces in consolidated PE-UHMW, different regions of PE-UHMW implants, and implants after *in vivo* use (explants). Anisotropy on the micrometer level cannot be evaluated by the presented toughness testing method; the results are discussed in 4.1 solely.

4.1 Comparison of the material states and correlation of structural parameters with mechanical properties

This chapter compares and discusses the mean values of structural parameters and mechanical properties of the material states are. The explant made from irradiation sterilized PE-UHMW (MAS) is splitted into two material states, bulk material and material in the highly oxidized region (see 4.2.1.6). Only the bulk material states are compared from other material states which show anisotropy (like RER, GAN and FIN; see 4.2). The data are given in Tables A.4.1-1 - 4, see Appendix. Furthermore, the dependencies of micro-mechanical properties and fracture toughness on the chemical structure, morphology and structural parameters at nanometer scale are discussed.

4.1.1 Chemical architecture of PE-UHMW

Ultra high molecular weight polyethylene is a homopolmer. After synthesis the polymer chains are nearly 100 % linear. During consolidation, the material undergoes an auto-crosslinking process. Besides $-CH_2$ - groups the material contains end groups in terms of $-CH_3$ - group or terminal vinyl unsaturations. In case the material is oxidized, degradation products can be analyzed. Irradiated PE-UHMW contains macro-radicals, tertiary C atoms, trans vinylene unsaturations additionally. The concentration of tertiary C atoms is very low even in crosslinked PE-UHMW. Hence their concentration and constitution (H- or Y- crosslinks) cannot be evaluated directly. A more detailed description of the chemical structure of PE-UHMW is given in 2.4.1.

First, the oxidative degradation in terms of OI (calculated from FTIR data, equation (21)) and normalized FTIR spectra is discussed. It is challenging to interpret the influence of OI on *in vivo* success of PE-UHMW. ASTM F 2102-06 [206] defines the OI value but it does not state limitations or describe the impact of OI on *in vivo* use of hip liners, other structural parameters, or mechanical properties. Kurtz [28] defines OI < 1 as low oxidation: despite evidence of oxidative degradation, it is unlike that these changes have a substantial negative impact on mechanical properties *in vivo*. An OI > 3 defines a critical oxidation – all mechanical integrity of PE-UHMW is lost. The region of 1 < OI < 3, moderate to severe oxidation, shows the greatest variability of mechanical properties. Therefore, statistical correlations of OI with mechanical properties determined by tests with miniature specimens scatter in this region.

Severe oxidative degradation is measured app. 1.8 mm below the surface which had contact with the synovial liquid in irradiation sterilized PE-UHMW explant (MAS ox, see 4.2.1.6). The other materials states show low oxidation (Figure 30).



Figure 30: Comparison of the investigated PE-UHMW material states, FTIR data: OI – oxidation index; OI of GUR 1020 and GUR 1020VitE is not analyzable

Ram extruded (RER), compression molded PE-UHMW (CMS, GUR 1020, GUR 1020VitE, and GUR 1050) and manufactured liners (1020ng and 1050ng) show lowest OI independently from molar mass. Consolidation and manufacturing (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng and 1050ng) cause no substantial bulk oxidative degradation as no distinct peak can be seen in the carbonyl region in the FTIR spectra (Figure 31). Some of the spectr, e.g. 1050ng in Figure 31, right show a wavy baseline in the carbonyl region. This kind of waviness empirically indicates that oxidative degradation is about to begin. The oxidation index OI calculated from these spectra according to ASTM F 2102 [206] is very low and shows high scattering. This kind of oxidative degradation can be introduced by mechanical and thermal stresses during sample preparation (e.g. microtoming [226]). It is not always possible to avoid this kind of damage.

Gamma – irradiation under inert atmosphere leads to the generation of long-living free radicals [110,117,118] in the polymer. These radicals reacted with oxygen from air as soon as available, i.e. after opening the packaging, during sample preparation, and measurements. Hence, the measured OI is higher in these material states (1020g and 1050g, Figure 30). A peak at 1720 cm⁻¹ and very small peaks at 1738 cm⁻¹ and 1705 cm⁻¹ can be found in the FTIR spectra of gamma-irradiated PE-UHMW (Figure 31, right). The peak at 1720 cm⁻¹ is associated with the keton- group. It results mainly from thermo-oxidative degradation [116]. The peak at 1738 cm⁻¹ is associated with the ester-group and results from mechano-oxidative degradation [119]. The peak at 1705 cm⁻¹ cannot be associated with a chemical group yet. The oxidation is low in these hip implants at the moment.

Nevertheless, oxidative degradation will occur *in vivo* easily. The long-living free radicals will further react with oxygen from the synovial liquid. In the explant MAS oxidative degradation of irradiation sterilized PE-UHMW preceded during *in vivo* use since the material was neither thermally treated in order to reduce free radicals nor protected by additives. A characteristic degradation profile developed (see 4.2.1.6). The corresponding normalized FTIR spectra of MAS bulk and MAS ox are shown in Figure 32, left (note the change in the scale of the y-axis).

Thermal treatment after irradiation reduces the concentration of free radicals in the material and the susceptibility to oxidation. The OI of radiation-crosslinked and remelted PE-UHMW

(Dsa and Lsa) is very low, similar to consolidated PE-UHMW (CMS, GUR 1020, GUR 1020VitE, and GUR 1050) and manufactured liners (1020ng and 1050ng; Figure 30). The FTIR spectra show a wavy baseline in the carbonyl region (Figure 32, right). The OI is higher in radiation-crosslinked and annealed PE-UHMW (X3TM, shelf aged - X3sa). A peak at 1720 cm⁻¹ is clearly visible in the FTIR spectra (Figure 32, right). This indicates that free radicals detectable in the material after the annealing procedure [84] react with oxygen as soon as it is available. In the case of X3sa, oxygen was available during sample preparation and measurements. In future investigations PE-UHMW containing free radicals, has to be stored, prepared and analyzed under well controlled conditions regarding surrounding atmosphere, temperature, exposure to light and storage time.

The bulk oxidative degradation of crosslinked PE-UHMW explants: In Durasul® it is not affected by *in vivo* use (explant GAN; no distinct peak at 1720 cm⁻¹, Figure 32). In contrast, the oxidative degradation in the explant made from X3 TM (FIN, bulk) is higher than in GAN and in the shelf aged X3 (X3sa, Figure 30). The FTIR spectra of the FIN bulk material show a peak at 1720 cm⁻¹ (Figure 32). The material further oxidized during *in vivo* use, sample preparation, and measurements in air.



Figure 31: Normalized FTIR spectra: left - consolidated PE-UHMW (RER bulk, CMS, GUR 1020, GUR 1020VitE, and GUR 1050); right - manufactured (1020ng and 1050ng) and gamma-sterilized (1020g and 1050g) liners



Figure 32: Figure 33: Normalized FTIR spectra: left - gamma-sterilized (1020g) and explant made from irradiation sterilized PE-UHMW (MAS bulk and MAS ox); right - radiation-crosslinked and remelted (Dsa, Lsa) and annealed (X3sa) liners and explants FIN and GAN (bulk material)



Figure 34: Comparison of the investigated PE-UHMW material states, FTIR data: TVI – trans vinylene index, TermVI – terminal vinylene index

Besides OI, there is another parameter describing structural characteristic of the polymer architecture - the TermVI semi-quantifies the concentration of terminal vinyl groups (equation (23)). This group is one of the possible end groups in polyethylene. The terminal vinyl groups react with PE-UHMW macro-radicals and form Y-crosslinks. Hence, the reduction of TermVI due to irradiation indicates Y-crosslinking mechanism in the polymer [113]. The calculation of TermVI from the FTIR spectra allows evaluation of trends. The peak is situated at 909 cm⁻¹. In this region the Fourier rippling complicates the semi-quantification. With this method differences in the concentration of terminal vinyl groups in PE-UHMW with different molar mass cannot be evaluated (Figure 34). The data show that the TermVI is higher in nonirradiated material states than in irradiated material states. The TermVI is exceptionally low in GUR 1050. This is further discussed in 4.1.7. Small but significant differences were found between the crosslinked material states: The TermVI in Durasul® (Dsa) is similar to the one in gamma-sterilized PE-UHMW (1020g, 1050g). The TermVI in Longevity TM (Lsa) is lower and in X3TM (X3sa) it is lowest. It probably indicates differences in the crosslinking state of the crosslinked PE-UHMW, although they were irradiated with similar total irradiation dose (see discussion of TVI).

The TVI is a measure for total irradiation dose and can be used as internal dosimeter [213] and it scales linearly with crosslink density up to a saturation level around 100 kGy [78]. It is lower in gamma-sterilized PE-UHMW than in crosslinked material. The findings correspond with total nominal irradiation dose of 25 kGy for the gamma-sterilized material states. The crosslinked material states were irradiated with total doses of 100 kGy (Lsa), 95 kGy (Dsa, GAN), and $3 \times 30 = 90$ kGy (X3sa, FIN). Despite this close range of total irradiation dose, the TVI is highest in Dsa and GAN, followed by Lsa, and X3sa and FIN showing lowest TVI. Muratoglu et al. [76] demonstrated that TVI scales linearly with total irradiation dose independently from temperature (below degradation temperature of PE-UHMW, ~ 300 °C). Nevertheless conditions during irradiation, sequential irradiation procedures, or thermal treatment after irradiation seem to influence the yield of trans vinylene unsaturations (and the consumption of terminal vinyl groups). Nevertheless, an unexpected low crosslink density in X3 TM (resulting from 90 kGy sequential irradiation) is reported in literature [84]. The reason for these differences has to be further elucidated. The TVI in MAS is higher than gamma-

sterilized samples but lower than in the crosslinked material states. Hence, the explant was irradiation sterilized prior to implantation. The TVI in explant MAS shows bigger scattering due to worse quality of the microtomed samples. Especially small cracks in the samples from oxidized material complicated FTIR measurements.

4.1.2 Dependencies of the degree of crystallinity on the chemical structure and physico-chemical treatment of PE-UHMW

One mayor influence on the degree of crystallinity is the molar mass as it governs chain mobility and diffusion in the melt. Furthermore, crystallinity is influenced by crystallization conditions (e.g. degree of super-cooling) and the thermal and mechanical history of the polymer.

First, molar mass influences the degree of crystallinity: GUR 1050 shows a lower degree of crystallinity (determined by FTIR and DSC, 1st heating run) than GUR 1020 in consolidated (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050) and manufactured material states (1020ng, 1050ng; Figure 35).



Figure 35: Comparison of the investigated PE-UHMW material states, degree of crystallinity calculated from FTIR data and DSC data

With higher molar mass the chains are more entangled in the higher viscous melt. The entangled (physically crosslinked) sections of the polymer chains cannot be incorporated in the regular structure of the crystallites during crystallization. Hence, the degree of crystallinity is reduced in material states with higher molar mass (Figure 36).



Figure 36: Correlation of the degree of crystallinity calculated from FTIR data with molar mass

Second, irradiation influences the degree of crystallinity: In the presence of oxygen chain scission dominates, in absence of oxygen crosslinking is favored. In any case long-lived radicals are generated in the crystalline phase which can migrate to the amorphous phase and react with oxygen during further live time of the PE-UHMW implant. Immediately after irradiation chains scission reactions release polymer chains (from all-trans non-crystalline interphase) which increase the degree of crystallinity and lead to a refinement of the lamellae. In the long term, oxidation products rearrange and together with further oxidation the crystallinity increases (see 2.4.2). These changes in the chemical structure of the polymer are reflected by the degree of crystallinity. The gamma-irradiation sterilized PE-UHMW liners (1020g, 1050g) show a higher degree of crystallinity compared to the non-irradiated PE-UHMW liners (1020ng, 1050ng). Obviously, the shortened chains recrystallize, but the effect of higher initial molar mass is still measurable: the degree of crystallinity is higher in GUR 1020g than in 1050g (Figure 35). Barron and Birkinshaw [70] found similar results. Nevertheless, the degree of crystallinity does not correlate with total irradiation dose in terms of TVI (Figure 37). Because third, thermal treatment after irradiation influences crystallinity: Remelting reduces the degree of crystallinity compared to the initial state of PE-UHMW. The free radicals form chemical crosslinks in the melt. These crosslinks cannot be incorporated in the crystalline phase during crystallization after the remelting procedure. Hence, the degree of crystallinity is lower in Durasul® (Dsa, GAN) and LongevityTM (Lsa; Figure 35). Beneficially, after remelting the concentration of free radicals is below detection limit [84] and hence, no oxidative degradation is measurable in shelf aged material (Dsa, Lsa) and after short time in vivo use (GAN). Annealing results in a higher degree of crystallinity compared to the initial state of PE-UHMW. The chain mobility is lower during annealing than during remelting. On the one hand this can be attributed to the temperature. On the other hand the existence of crystallites during annealing hinders reptation. During annealing unmodified sections of the polymer chain attach to the crystallites (which bring themselves to more perfection due to enhanced chain mobility at temperatures much higher than room temperature). Presumably,

there is a competition between crosslinking and crystal growth which finally results in a higher degree of crystallinity in X3TM (X3sa, FIN; Figure 35). Unfavorably, after annealing the concentration of remaining free radicals is low but above detection limit [84] and oxidative degradation is measurable in shelf aged hip implants (X3sa) and after *in vivo* use (FIN). The effect of initial molar mass on the degree of crystallinity is not measurable in the crosslinked material states (Dsa, Lsa, X3sa, GAN, FIN).



Figure 37: Correlation of the degree of crystallinity calculated from FTIR data with TVI

Fourth, oxidative degradation influence the degree of crystallinity: Crystallinity correlates linearly with OI, as shown with data from explant MAS (Figure 38): the higher the OI the higher the degree of crystallinity. The oxidation of the polymer chains leads to recrystallization of the shortened chains. The degree of crystallinity rises. Similar results were found in other oxidized PE-UHMW material states [223].



Figure 38: Correlation of the degree of crystallinity calculated from FTIR data with OI – oxidation index of *in vivo* used explant made from irradiation sterilized PE-UHMW (MAS)

In vivo use did not influence bulk crystallinity in the investigated retrievals. The degree of crystallinity is similar in shelf aged virgin implants compared with explants made from the same PE-UHMW type (Dsa and GAN; X3sa and FIN; 1020g/1050g and MAS; Figure 35).

4.1.3 Morphology and structural parameters at nanometer scale

The degree of crystallinity is a very important structural parameter which influences the mechanical properties of semi-crystalline polymers. Nevertheless, a more detailed knowledge of the polymer morphology and the amorphous phase is necessary to understand the influence of structural parameters on the mechanical properties in semi-crystalline polymers [224]. In this chapter, structural parameters in PE-UHMW (besides degree of crystallinity) are discussed.

Generally, the melting behavior in DSC experiments reflects physical history and chemical structure of the polymer in the first heating run and the chemical structure in the second

heating run (due to the same thermal crystallization conditions in the controlled DSC cooling run for all samples). The melting point in DSC experiments reflects the average lamellar thickness [217] (equation 27).

Differences in the melting point calculated from the first and the second heating run between the non-irradiated material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) are within the precision of the DSC method (≤ 1 °C, Figure 39). Hence, differences in average lamellar thickness l_c in these material states should not be interpreted too (Figure 40). Generally, the crystallite thickness l_c is in the same range as reported for PE-UHMW by other authors [113,151,225] and evaluated with other experimental methods like small angle X-ray scattering (SAXS) [70].



Figure 39: Comparison of the investigated PE-UHMW material states, DSC data: melting point in the first (T_{m1}) and second heating run (T_{m2}) , minimum temperature during crystallization (T_c) and temperature at the beginning of the crystallization $(T_{c, onset})$

The T_{m1} is higher in the gamma-sterilized material states (1020g, 1050g) than in the nonirradiated material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng; Figure 39). Similar effect of irradiation-sterilization on T_{m1} is reported by Premnath et al. [150]. The authors claim the hindrance of the melting process due to crosslinks in the amorphous phase to be the reason of this effect. But irradiation leads to thickening of the lamellae due to release and recrystallization of scissioned polymer chains [148-150]. The melting endotherm describes essentially the crystalline phase. The amorphous phase has minor influences on this endotherm. Therefore, the reason of the higher T_{m1} is predominantly attributed to chain scission and recrystallization in gamma-sterilized PE-UHMW (1020g, 1050g). Hindrance of the melting process by crosslinks can result in broadening of the melting endotherm (e.g. in Lsa)

The melting point calculated from the second heating run (T_{m2} , Figure 39) is lower in gammasterilized PE-UHMW compared with non-irradiated material states. The result further indicates reduction in molar mass resulting from the irradiation process (as previously indicated by degree of crystallinity; see discussion of the crystallization process). Differences of 6 °C in the DSC melting points calculated from the first and the second heating run of gamma-sterilized PE-UHMW components were also reported by [225]. The authors give no explanation of these results. The difference probably indicates that chain scission altered the crystallization behavior.

The T_{m1} and T_{m2} are higher in crosslinked and thermally treated material states (Dsa, Lsa, X3sa, GAN, FIN) compared with non-irradiated material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) due to higher molar mass. As a consequence from thermal treatment, average lamellar thickness l_c (Figure 40) are lower in the remelted hip implants (Dsa, GAN, Lsa) than in annealed hip implants (X3sa, FIN). The calculation of l_c using Thomson-Gibbs equation (equation 27) gives high values for Durasul® (Dsa, GAN), since the melting endotherm is a double peak in this material state and l_c is calculated from the higher melting peak (see lamellar thickness distribution). The higher T_{m2} indicates higher molar mass due to crosslinking compared with non-irradiated material states. The effect of annealing is not reflected in the second DSC heating run. The melting endotherm is broadened due to crosslinks in the amorphous phase, but the peak itself is in the same temperature range. The underlying changes in chemical structure are discussed together with the lamellar thickness distribution.

No differences in the peak melting temperatures were found between virgin implants Dsa and X3sa, and *in vivo* used explant GAN and FIN. The results of MAS (bulk and ox) cannot be fully elucidated yet: the T_{m2} is higher than in gamma-sterilized virgin implants (1020g, 1050g) and it is higher in the oxidized material (MAS ox) compared with bulk material. Maybe the higher total irradiation dose (compared with 1020g and 1050g) and the scattering of the absorption throughout the material result in this melting behavior. These results should be approved by further investigations of molar mass but this is not a trivial task in consolidated PE-UHMW [2].



Figure 40: Comparison of the investigated PE-UHMW material states, DSC data: average lamella thickness l_c calculated from the first DSC heating run (equation 27)

In the PE-UHMW melt preordered domains are proved [68,146]. They exist due to the low mobility of the very long polymer chains. Generally, immobilization changes crystallization kinetics and is favorable to the nucleation step in the crystallization [136]. In PE-UHMW the crystallization starts at higher temperatures compared with PE-HD. A lower degree of super-

cooling is necessary to start the crystallization of PE-UHMW melt when it is cooled down during production processes and in the DSC experiment.

The crystallization temperature T_c and temperature at the beginning of the crystallization $T_{c, onset}$ give information on the crystallization behavior, preordered domains and the mobility of the melt.

 T_c and $T_{c, onset}$ differ between non-irradiated material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) within the precision of the method (≤ 1 °C, Figure 39). Oral et al. [203] showed that vitamin E acts as plasticizing agent in high pressure crystallization of PE-UHMW containing 0.1 %wt, 0.2 %wt, and 0.3 %wt vitamin E leading to higher degree of crystallinity. $T_{c, onset}$ is slightly lower in GUR 1020VitE crystallized at atmospheric pressure (Figure 41, left) and the degree of crystallinity slightly higher (Figure 35). These results agree with the findings by Oral et al. [203], but they should not be over-interpretated due to limitations of the DSC method.

The gamma-sterilized PE-UHMW (1020g, 1050g) shows significantly higher $T_{c, onset}$ and similar T_c compared with non-irradiated material states. This increase in $T_{c, onset}$ can be attributed to crosslinks which hinder reptation ("lengthwise" diffusion) of the polymer chains. The chemical bond is much more stable than van der Waals interaction of the polymer chains and enables disentanglement. Preordered domains dissolve worse in the melt. Hence, the crystallization starts at higher temperatures than in non-irradiated PE-UHMW.

The results indicate that both, chain scission (higher T_{m1} and l_c) and crosslinking (higher $T_{c, onset}$) took place during irradiation under nitrogen atmosphere (as well as shelf aging and measurements). Which chemical reaction dominates cannot be deduced from the DSC data. The changed crystallization behavior is reflected in lower T_{m2} .

Crosslinking and thermal treatment further reduces the mobility of the melt. The crosslinked material states (Dsa, Lsa, X3sa, GAN, FIN) show higher T_c and $T_{c, onset}$ (Figure 39). The preordered domains are caged by Y-crosslinks in a 3D polymer network. A sketch is given in Figure 37, right. T_c and $T_{c,onset}$ are highest in Durasul® (Dsa, GAN)and lowest in X3TM (X3sa, FIN). This indicates that the immobilization of the melt due to crosslinking is affected by conditions during irradiation, thermal treatment and the sequential crosslinking process. No differences were found between virgin implants Dsa and X3sa, and *in vivo* used explants GAN and FIN.



Figure 41: Crystallization behavior - DSC cooling runs, T_c ... crystallization temperature, $T_{c, onset}$... temperature at the beginning of the crystallization (left) and schematic presentation of preordered domains caged by Y-crosslinks in the 3D polymer network of crosslinked PE-UHMW (right)

Oxidative degradation reduces molar mass, the polymer chains become more mobile in the melt, and preordered domains are not that stable anymore. The crystallization starts at lower temperatures (lower $T_{c, onset}$) in MAS ox than in MAS bulk samples (Figure 39). The T_c of MAS bulk and MAS ox samples do not show this trend.

 $T_{c, onset}$ reflects changes in the chain mobility in the polymer melt due to crosslinking and reduction in molar mass more sensitive than T_c . Therefore, in this Thesis $T_{c, onset}$ is used to evaluate the mobility of PE-UHMW melt. Above the glass transition temperature, the molecular interactions determining the properties of the non-crystalline state are similar in nature (the absolute values of the interacting forces depend on temperature). Hence, the $T_{c, onset}$ is used as a characteristic value reflecting the chain mobility in the amorphous phase at ambient temperature.

The lamellar thickness distribution (LTD) gives more detailed information on the morphology of the PE-UHMW material states. The LTD was calculated from the first and the second DSC heating runs (equation 32, see 3.3.2). Peaks at very low lamellar thickness (< 5 nm) are negligible due to limitations of DSC measurements (polymer related heat flow cannot clearly be distinguished from baseline fluctuations).

No substantial differences are found between the LTD of ram extruded (RER) and compression molded (CMS) PE-UHMW, material states with different molar mass and vitamin E (GUR 1020, GUR 1020VitE, GUR 1050) and manufactured liners (1020ng, 1050ng). The LTD calculated from both heating runs show a single maximum (centered around 21 nm in the first heating run and around 18 nm in the second heating run, Figure 42). Generally, the LTD of the samples calculated from the second heating run is narrower and the maxima are shifted to lower values compared with the LTD calculated from the first heating run due to the controlled DSC cooling run [70,148].



Figure 42: Comparison of non-irradiated PE-UHMW material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng); LTD calculated from the first (left) and second (right) DSC heating runs

Figure 43 shows the LTD of gamma-sterilized (1020g, 1050g) and radiation crosslinked PE-UHMW hip implants (Dsa, Lsa, X3sa). Based on the LTD of the non-irradiated material states (e.g. 1020ng, 1050ng), the effects of gamma-sterilization, irradiation crosslinking and thermal treatment are discussed and the underlying mechanisms are elucidated for the LTD calculated from the first heating run:

 Gamma-irradiation (1020g, 1050g) leads to thickening of the preexisting lamellae due to enhanced mobility of scissioned polymer chains. The all-trans non-crystalline interface releases chains for further crystallization due to chain scission. The maximum in LTD calculated from the first heating run is shifted to higher values (app. 23.9 nm in 1020g compared with 21.5 nm in 1020ng and 22.1 nm in 1050g compared with 19.5 nm in 1050ng) and there are more lamellae sized between 30 - 40 nm in 1020g and 1050g compared with 1020ng and 1050ng. Even more lamellae sized between > 30 nm can be observed in crosslinked PE-UHMW (Dsa, Lsa, X3sa) too, but in these material states the thermal treatment after irradiation influences the LTD in addition.

- Upon gamma-irradiation a second population of crystal lamellae emerges (around 10 15 nm). Material released too distant from the original lamellae or prevented by steric factors (i.e. crosslinks) builds new lamellae. Their size is limited by the crosslinks and entanglements in the amorphous phase presumably. This effect is more pronounced in 1020g than in 1050g and can be observed in Dsa and Lsa too. No distinct second population of smaller lamellae is found in X3sa. The smaller sized lamellae populations have been observed in irradiated PE-UHMW by Barron and Birkinshaw [70,148] and Premnath et al [150] too.
- Crosslinks formed during irradiation cannot be incorporated in the crystallites and hinder the formation of larger crystallites during crystallization. This effect can be observed when comparing the LTD calculated from the second heating run: In 1020g and 1050g the maxima are at lower lamellar thickness (around 15.8 nm) compared with 1020ng and 1050ng (maxima around 18 nm). Remelting (Dsa, Lsa) after irradiation involves the same effect: high fraction of very small lamellae and a broadened peak at bigger lamellae fractions can be found.
- Irradiation at higher temperature leads to a distinct bimodal LTD (peaks at 30 nm and 9 nm) in Durasul® (Dsa): During irradiation at 120 °C the small and imperfect lamellae melt. The bigger lamellae thicken due to annealing effects. This morphology of the partially melt PE-UHMW is persevered by crosslinks formed in the amorphous part. In the remelting step the remaining crystal lamellae melt and the macro-radicals are terminated by forming additionally crosslinks. Nevertheless, there are preordered domains in the melt and their melting is hindered by the crosslinks. The crystallization from the structured melt forms the bimodal LTD observed. In LongevityTM (Lsa) no bimodal LTD can be seen: During the irradiation with electron beam the radicals are formed statistically homogenous in the amorphous and crystalline phase leading to crosslinking and chain scission simultaneously. Remelting enables further crosslinking in the melt. During crystallization lamella growth is hindered by crosslinks spread allover the material. A LTD with broadened mono-modal distribution emerges.
- In X3TM (X3sa) irradiation at ambient temperature generates radicals in the amorphous and crystalline phase of the PE-UHMW leading to crosslinking and chain scission. The subsequent annealing step reduces free radicals due to further crosslinking and movement of the radical site along the polymer chain in the crystalline phase. Additionally, annealing drives lamellae towards thermodynamic equilibrium and leads to thickening of the lamellae and refinement of crystal structure (reflected by higher fractions of thick lamellae). Since irradiation and annealing are repeated three times, some of the lamellae become thicker and thicker and the amorphous phase contains more crosslinks every irradiation step. Hence, very thick lamellae (app. 33 70 nm) and only small crystallites (< 15 nm) can be found in X3sa as the crosslinks of the amorphous phase cannot be incorporated in the crystallites.</p>

Generally, the first DSC heating run gives information on the morphology based on chemical structure, thermal and mechanical treatment and ageing. The second heating run reflects the morphology based on the chemical structure only. Comparing the LTD calculated from the first and the second heating run elucidates if the morphology in "locked in" by the chemical structure (Dsa, Lsa) or if it is a result of physical treatment (1020g, 1050g, X3sa):

- The morphology generated by irradiation is not "locked in" by the crosslinks in gammasterilized material (1020g, 1050g). No thermal treatment after irradiation stabilized these material states. The crosslinks favor the nucleation step during crystallization and hinder formation of bigger lamellae. Hence, the maxima in LTD calculated from the second heating run are shifted to lower values compared with non-irradiated material states (1020ng, 1050ng).
- Durasul® (Dsa) exhibits a bimodal LTD calculated from the first and second heating run, indicating that the underlying effects are chemical in nature: The morphology generated during crosslinking process is "locked in". The same applies for LongevityTM (Lsa).

• In X3TM (X3sa) the LTD calculated from the second heating run the effects of annealing are not reflected: a double peak with maxima at 10 and 13 nm declines to zero at app. 40 nm. This LTD is base on the chemical structure of X3 with the crosslinks favoring nucleation step and hindering the crystal growth. The morphology generated by stepwise irradiation and annealing is not "locked in" by the chemical structure

In vivo use had no substantial influences on the LTD of explants GAN, FIN, and MAS (Figure 44). The LTDs calculated from the first and the second DSC heating run are very similar for Dsa and explant GAN, and X3sa and explant FIN. Minor differences exist between virgin gamma-sterilized PE-UHMW liners (1020g and 1050g) and MAS (bulk and oxidized region): in MAS (bulk and ox) the maximum is shifted to higher lamellar thickness in the LTD calculated from the second heating run. This indicates differences in chemical structure which are probably related with oxidative degradation and rearrangement of the degradation products during time *in vivo*, and the slightly higher TVI. The differences in LTD cannot be fully elucidated since the initial state of the liner, its thermo-mechanical history, and its biochemical exposure is not known in detail.



Figure 43: Comparison of gamma sterilized PE-UHMW (1020g, 1050g) and crosslinked PE-UHMW (Dsa, Lsa, X3sa); material states 1020ng and 1050ng are included for comparison reasons; LTD calculated from the first (left) and second (right) DSC heating runs



Figure 44: Comparison of *in vivo* used PE-UHMW material states, LTD calculated from the first (left) and second (right) DSC heating runs

The mechanical interactions of crystalline and amorphous phase are governed by tie molecules and entanglements of the polymer chains. The probability of occurrence of tie molecules and tie molecule and entanglement area fraction at the crystal-amorphous interface were calculated from DSC data (according to equations (1) and (13)). Two basic assumptions were made: First, the polymer chains are crosslinked via Y-crosslinks (the reduction in TermVI confirms that this crosslinking mechanism occurs) and Y-crosslinking is regarded similar to long chain branching. Second, polymer degradation is negligible (MAS ox was excluded).

The probability of occurrence of tie molecules p is between 0.304 (in Dsa) and 0.325 (in RER) for all material states except $X3^{TM}$ (X3sa, FIN; Figure A.4.1-1, see Appendix). In $X3^{TM}$ the probability of occurrence of tie molecules is lower (X3sa: 0.270, FIN: 0.274). This is related with the annealing process resulting in higher average lamellar thickness in this material.

Table 7: Comparison of characteristic structural parameters PE-UHMW ^{a)} and literature data from
PE-HD ^{b)} , ethylene-hexene copolymer ^{c)} , and ethylene homopolymer and ethylene-octene copolymer ^{d)} ;
p probability of occurrence of tie molecules in polyethylene, F _s tie molecule area fraction at the
crystal-amorphous interface calculated from the first DSC heating run

	this Thesis ^{a)}	Beerbaum [138]	Huang, Brown [137] Seguela [136] ^{c)}	Patel [142] ^{d)}
molar mass (g/mol)	$3.5 - 5.7 \times 10^{6}$	$9-55 \times 10^{4}$	$1.3 - 1.7 \times 10^5$	$2 - 9.9 \times 10^4$
average lamellar thickness (nm)	22.4 - 40.9	10.5 - 28.7	17 - 33	3.1 - 30
degree of crystallinity (%)	47.9 - 65.5	58.3 - 81.1	52 - 71	14 - 72
р	0.304 - 0.325	0.06 - 0.24	0.002 - 0.093	0-0.25
F _s	0.491 - 0.733	-	0.005 - 0.160	

Compared with the literature data for PE-HD (Table 7) from Beerbaum [138] and Patel [142], the PE-UHMW material states show little variations in the probability of occurrence of tie molecules p (X3sa and FIN excluded). No data concerning p in PE-UHMW were found in literature.

The probability of occurrence of tie molecules reaches a plateau in ultra high molar mass region of PE (molar mass > 10⁶ g/mol; Figure 45). Differences in molar mass, in average lamellar thickness and the degree of crystallinity nearly compensate each other in their effects upon p compared with PE-HD and PE copolymers [138,142]. Within the non-crosslinked PE-UHMW material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050) p is slightly higher in higher molar mass PE-UHMW types (Figure A.4.1-1, see Appendix). Nevertheless, p does not correlate with the degree of crystallinity and l_c (Figure A.4.1-2 and Figure A.4.1-3, see Appendix). Gamma-sterilization (1020g, 1050g) and irradiation crosslinking combined with remelting (Dsa, Lsa) have little influence on the probability of occurrence of tie molecules. At molar mass higher than app. 1×10^6 g/mol many segments of the very long and entangled chains attach too nearby lamellae or form entanglements. Hence, an increase (due to synthesis or crosslinking) or a decrease (due to chain scission) in molar mass in the region > 1 $\times 10^6$ g/mol does not influence the probability of occurrence of tie molecules anymore (at comparable thermal crystallization conditions) substantially.



Figure 45: Comparison of p – the probability of occurrence of tie molecules in polyethylene (data from literature and PE-UHMW); material states with degrees of crystallinity closest to 60 % are depicted

The concentration of "junction points" in the material, which can be actually related to the degree of crystallinity, can be considered in the evaluation of tie molecules additionally [142]. The model proposed by Seguela [136] includes the crystal volume fraction and chain overlapping in real polymers (see 2.4.2). The density of mechanically active molecular species - tie-molecules and entanglements - in the amorphous phase that bridge neighboring crystallites is calculated as area fraction at the crystal-amorphous interface F_s (equation 13). Data concerning entanglement area fraction at the crystal-amorphous interface (equation 14) is not calculated due to the lack of literature data which allow confirmation.



Figure 46: Comparison of the investigated PE-UHMW material states, DSC data: F_s – tie molecule area fraction at the crystal-amorphous interface calculated from the first DSC heating run

The F_s data calculated from PE-UHMW material states is given in Figure 46. Since the p – values are very similar for the non-crosslinked material states, the tie molecule and entanglement area fraction at the crystal-amorphous interface (F_s) increases with the degree of crystallinity (Figure A.4.1-4, see Appendix). The F_s value for GUR 1020 containing Vitamin E
(0.600) is slightly higher than the other values from consolidated material states (0.566 – 0.580 in RER, CMS, GUR 1020 and GUR 1050). F_s is higher in manufactured PE-UHMW liners (1020ng, 1050ng) compared with the consolidated material states (RER, CMS, GUR 1020, GUR 1020VitE and GUR 1050). Gamma sterilization further increases F_s in virgin implants (1020g, 1050g) as well as in explant MAS Lower F_s - values are calculated for the shelf aged liners made from Durasul® and LongevityTM (Dsa, Lsa). In the crosslinked material states F_s is highest in X3TM (X3sa, FIN) the low value of p in combination with high degree of crystallinity results in similar F_s – values compared with consolidated PE-UHMW.

A schematic presentation of the nano-structure of PE-UHMW based on the results from calculation of tie molecule and entanglement area fraction at the crystal-amorphous interface is given in Figure 47. $F_s > 0.5$ means that more than half of the polymer chains emerging from the crystal surface do not fold tight to attach at an adjacent site in the crystal but form tie molecules or entanglements. These molecules contribute to the all-trans non-crystalline interphase.



Figure 47: Schematic presentation of the nano-structure of PE-UHMW based on the results from calculation of tie molecule (red) area fraction at the crystal-amorphous interface (pictured $F_s \sim 0.5$); TM ... tie molecule, E ... entanglement, C ... crosslink; distribution of amorphous and crystalline phase is not drawn according to their actual proportions in PE-UHMW

Comparison of F_s – data with literature is not possible since the data calculated by Seguela [136] is very low due to the low p – values evaluated by Huang and Brown [137] for their polymer systems and no other literature data is available yet. The influence of the tie molecule and entanglement area fraction at the crystal-amorphous interface on mechanical properties is discussed in chapter 4.1.5 and 4.1.7.

4.1.4 Micro-mechanical properties

Depth sensing indentation testing is a quasi-non-destructive material testing method. It was used to examine the micro-mechanical properties hardness and indentation modulus (see 3.4.1) on micrometer scale.

The mean values of all measurements for all material states are shown in Figure A.4.1-5 and Figure A.4.1-6 (see Appendix). The hardness and the indentation modulus is higher in GUR 1020 (GUR 1020, GUR 1020VitE, 1020ng, 1020g) than in GUR 1050 (RER, CMS, GUR 1050, 1050ng, 1050g). Gamma-sterilization (1020g, 1050g) leads to significantly higher values of H_{IT} and E_{IT} compared with non-irradiated material states (e.g. 1020ng, 1050ng). The micromechanical properties are reduced in crosslinked and remelted material states (Dsa, Lsa and GAN) whereas they are elevated in crosslinked and annealed material states (X3sa and FIN) compared with non-irradiated material states (e.g. 1020ng). The explant MAS shows very high values of H_{IT} and E_{IT} in the highly oxidized region (MAS ox), the values of bulk material (MAS bulk) are similar to gamma-sterilized material states (1020g, 1050g).

Both micro-mechanical properties, H_{IT} and E_{IT} , are lower in GUR 1020 containing vitamin E (GUR 1020VitE) than in GUR 1020 despite slightly higher degree of crystallinity (determined by DSC). A possible reason can be a plasticizer effect of vitamin E, but this reason might be

unlikely due to the very low plasticizer-concentration (0.1 %wt vitamin E) in the polymer. E. Oral et al. [203] showed an increase in degree of crystallinity (determined by DSC) in GUR 1050 containing 0.1 %wt vitamin E too. Mechanical properties like ultimate tensile strength and yield strength, are not affected by additivation with 0.1 %wt vitamin E in this study. The reasons for the lower values of H_{TT} and E_{TT} have to be further elucidated.

4.1.5 Dependency of micro-mechanical properties on structural parameters

The micro-hardness and indentation modulus correlate with the degree of crystallinity, as can be seen in Figure 48 and Figure 49. H_{IT} and E_{IT} increase with increasing degree of crystallinity. Micro-hardness and indentation modulus are influenced by molar mass indirectly (Figure A.4.1-7 and Figure A.4.1-8, see Appendix) - higher molar mass leads to lower degree of crystallinity in non-crosslinked materials states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) and the degree of crystallinity influences H_{IT} and E_{IT} : Higher degree of crystallinity correlates with higher micro-hardness and indentation modulus (Figure 48 and Figure 49).



Figure 48: Correlation of H_{IT} - micro hardness with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states (MAS ox excluded)



Figure 49: Correlation of E_{IT} – indentation modulus with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states (MAS ox excluded)

The same applies for oxidatively degraded PE-UHMW: The oxidized region of the explant MAS (MAS ox) was excluded from the correlation depicted in Figure 48 and Figure 49. The local hardness and indentation modulus data is correlated to the local degree of crystallinity in the explant MAS (Figure 50). The micro-mechanical properties increase linearly with increasing degree of crystallinity. Radiation-sterilization leads to oxidative degradation during *in vivo* use. The shorter polymer chains recrystallize and this results in a higher degree of crystallinity (see 4.1.2, Figure 38). Hence, higher micro-hardness and indentation modulus are measured in the area of elevated degree of crystallinity and oxidative degradation. This correlation shows that DSI technique is a adequate method for characterization of mechanical properties of oxidized PE-UHMW. As this method uses very small sample volumes, only low scattering of the characteristic values is observed.



Figure 50: Correlation of H_{IT} – micro-hardness (left) and E_{IT} - indentation modulus (right) with the degree of crystallinity calculated from FTIR data in explant MAS

The elastic modulus depends to a large extend on the degree of crystallinity in semi-crystalline polymers. It is not governed by lamellar thickness [224]. This applies for the PE-UHMW material states: E_{IT} (Figure 51) and H_{IT} (Figure A.4.1-9, see Appendix) do not depend on average lamellar thickness l_c .

Nevertheless, the LTD influences the micromechanical properties in addition especially in crosslinked PE-UHMW. In literature [14,15,186] it is believed that a higher number of smaller fragmented lamellae in crosslinked PE-UHMW reduces the tensile elastic modulus. The lamellar thickness distributions (calculated from the first heating run, Figure 43) show higher fractions of small lamellae in Dsa, Lsa, and gamma-sterilized PE-UHMW (1020g, 1050g) whereas X3sa does not show these small lamellae. The indentation modulus is higher in X3sa than in Dsa and Lsa. This can be attributed to the higher degree of crystallinity and to the differences in LTD (it does not disprove the effect of small fragmented lamellae on the elastic properties). When X3sa and gamma-sterilized PE-UHME (1020g, 1050g) are compared it is obvious that the small lamellae in the irradiation sterilized material lead to a reduction in E_{IT} and H_{IT} at similar levels of crystallinity. From a technological point of view annealing after irradiation preserves the elastic properties of PE-UHMW better than remelting because of the generation of small lamellae is abolished.



Figure 51: Correlation of EIT - indentation modulus (right) with lc - average lamellar thickness

The effect of crystallinity on the micro-mechanical properties dominates: No correlation is observed between E_{IT} and H_{IT} with TermVI (Figure A.4.1-10 and Figure A.4.1-11, see Appendix) and the temperature at onset of crystallization $T_{c,onset}$ (Figure A.4.1-12 and Figure A.4.1-13, see Appendix) as well as the probability of occurrence of tie molecules p (Figure A.4.1-14 and Figure A.4.1-15, see Appendix) and the tie molecule area fraction at the crystal-amorphous interface F_s (Figure A.4.1-16 and Figure A.4.1-17, see Appendix). Hence, H_{IT} and E_{IT} are not influenced by the mobility of the amorphous phase (reflected by TermVI and $T_{c,onset}$) and the concentration of mechanically active molecular species.

4.1.6 Results form fracture toughness testing

The results calculated from J-R experiments are shown in Figures A.4.1-18 – 28, see Appendix. According to ASTM D 6068 [188] representative J-R curves in Figure 52 are depicted as power law regression lines which obey $J = C_1 \Delta a^{C_2}$ (with C₁ and C₂ being fitting parameters).



Figure 52: Comparison of the investigated PE-UHMW material states – representative J-R curves (power law regression lines)

The non-irradiated material states show toughest behavior: the slope of the J-R curves is highest. In literature GUR 1020 is described as being tougher than GUR 1050 in terms of impact toughness [24]. This behavior shows up in the compression molded material states

(with GUR 1020 and GUR 1020VitE exhibiting higher resistance against crack growth than GUR 1050). It is not obvious when compared with 1050ng which shows similar J-R behavior as GUR 1020. Also, the manufactured hip implants made from GUR 1050 (1050ng) show tougher behavior than the ones made from GUR 1020 (1020ng). Therefore, within the scope of this Thesis consolation method, molar mass, additivation by vitamin E and manufacturing does not systematically influence the J fracture behavior.

The J-R curves of 1020g and 1050g have a lower slope. Gamma-irradiation reduces the J fracture toughness coming down from a basic toughness level: As in 1050ng and 1020ng, the 1050g is tougher than 1020g. Similar J-R behavior of gamma-sterilized GUR 1020 and GUR 1050 was evaluated by Varadarajan et al. [196] too.

Irradiation crosslinking further reduces the toughness of PE-UHMW and changes the shape of the J-R curves (indicating different fracture behavior). The resistance against stable crack growth is reduced in the crosslinked hip implants (Dsa, Lsa, X3sa). The toughness is affected by the thermal treatment after irradiation: annealing (X3sa) preserves the resistance against stable crack growth better than remelting (Dsa, Lsa). Qualitatively similar results for crosslinked PE-UHMW material states have been published [195-197]. The temperature during irradiation does not affect the fracture behavior (compare Dsa with Lsa). The differences in the fracture behavior can be attributed to different crosslinking states in the amorphous phase. Thermal treatment after irradiation increases the network density in the amorphous phase as additional crosslinks are formed. These changes are reflected by the changes in the shape of the J-R curves of crosslinked hip implants (Dsa, Lsa, X3sa) compared to J-R curves of gammasterilized implants (1020g, 1050g).

The fracture surface of the specimens (after cooling them in liquid nitrogen and breaking) was evaluated by scanning electron microscopy (SEM). The fractographs of all material states are shown in Figure 53.

The fracture surfaces of the non irradiated material states show diamond pattern in the region of stable crack growth (Figure 53, a and c). This pattern is charcateristically observed in PE-UHMW [201,18]. Opposite to PE-HD [138], PE-UHMW lacks cavitations (formation of voids) in front of the crack tip, as can be seen in Figure 54, aIII. The material in the process zone is highly streched (Figure 54, b). Hence, stable crack growth in PE-UHMW is linked to the intrinsic viscoelastic behavior of the material itself [204]. At the crack tip the material is stretched till it fails. These tearing lines are observed as diamond pattern on the fracture surface [187]. The gamma-sterilized material states (1020g, 1050g) show no diamond pattern (Figure 53, b and d). This indicates a change in the plastic strain behavior of the material states.

The irradiation crosslinked and remelted PE-UHMW samples (Dsa, Lsa; Figure 53, e and f) show diamond pattern but at larger scale than in non-irradiated PE-UHMW whereas the irradiation crosslinked and annealed PE-UHMW sample (X3sa; Figure 53, g) does not show a diamond pattern but tearing lines can be observed. The small lines perpendicular to the crack growth direction result from relaxation processes (during and) after the fracture testing.

Similar material behavior was observed by Simis et al. [201] and Baker et al. [18] in irradiated PE-UHMW.



Figure 53: Comparison of the investigated PE-UHMW material states, data frature mechanical testing: fractographic investigations (SEM, \times 500; crack growth direction is left to right in the pictures); a – 1050ng, b – 1050 g, c – 1020ng, d – 1020g, e – Dsa, f – Lsa, g – X3sa

The lack of extrinsic phenomena like cavitation contributes to the unique fracture properties of PE-UHMW [204]. The different interaction of a crack tip with PE-UHMW results in other dependencies on structural parameters than in PE-HD, as will be discussed in 4.1.7.



Figure 54: a) Area of stable crack growth II; area in front of the crack tip III (example: 1050g; crack direction was from left to right in the pictures); b) scheme of crack tip and process zone in PE-UHMW

The crack growth behavior does not allow the evaluation of the physical crack initiation. Hence, the technical crack initiation value $J_{0,2}$ is used in approximation as characteristic value

for comparison and correlation to structural parameters (see 3.4.2.2). The stable crack growth behaviour $dJ/d\Delta a|_{0.2}$ is evaluated by calculation of the derivative of the J-R curve at crack extension $\Delta a = 0.2$ mm (see 3.4.2.2).

Figure 55 and Figure 56 show the $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ values of all materials states. These values are significantly higher in non irradiated material states (RER, GUR 1020, GUR 1020VitE, GUT 1050, 1020ng, 1050ng) than in irradiated ones (1020g, 1050g, Dsa, Lsa, X3sa).

RER, GUR 1020, and GUR 1020VitE show higher $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ than GUR 1050. The data is qualitatively consistent with data from double notched Izod test of these lots of PE-UHMW (provided by Orthoplastics; Figure A.4.1-29, see Appendix). In manufactured and gamma-sterilized hip implant GUR 1050 (1050ng, 1050g) shows a higher $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ values than GUR 1020 (1020ng, 1020g; no lot data for comparison available).



Figure 55: Comparison of the investigated PE-UHMW material states, data fracture mechanical testing: $J_{0.2}$ – technical crack initiation value = value of the J-Integral at crack extension of 0.2 mm (kJ/m²)

The resistance against crack initiation is similar in gamma-sterilized PE-UHMW (1020g, 1050g) and crosslinked implants (Dsa, Lsa, X3sa). Whereas the resistance against stable crack growth is higher in gamma-sterilized PE-UHMW (1020g, 1050g) than in crosslinked implants (Dsa, Lsa, X3sa). This result reflects the changed fracture behavior and will be further discussed in 4.1.7. The J_{0.2} and dJ/d Δa |_{0.2} values of the radiation crosslinked and remelted hip implants (Dsa and Lsa) are similar. The J_{0.2} and dJ/d Δa |_{0.2} value of the radiation crosslinked and annealed hip implants (X3sa) is significantly higher than in Das and Lsa. Again, these results agree qualitatively with literature data on similar crosslinked PE-UHMW material states [195-197].



Figure 56: Comparison of the investigated PE-UHMW material states, data fracture mechanical testing: $dJ/d\Delta a | 0.2 - measure$ for stable crack growth (× 1000 kJ/m³)

4.1.7 Dependency of characteristic toughness value $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ on structural parameters

In PE-UHMW the toughness increases up to a molar mass of app. $2 - 3 \times 10^6$ g/mol and then decreases with higher molar mass [3,24]. Fracture toughness dos not show a dependency on molar mass in the material states tested in this Thesis. Neither in non-crosslinked materials states nor in crosslinked material states J_{0.2} and dJ/d Δa |_{0.2} correlates with (initial) molar mass (Figure A.4.1-30 and Figure A.4.1-31, see Appendix). Probably, the number of material states tested is too low to reveal a correlation.

In contrast to micromechanical properties, $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ are not directly influenced by the degree of crystallinity in the PE-UHMW. Figure 57 and Figure 58 show that non-irradiated material states have higher fracture toughness than irradiated material states. Even if both groups are considered as different materials none of these material clusters correlates with the degree of crystallinity (Figure A.4.1-32 and Figure A.4.1-33, see Appendix).

Non-irradiated material states (RER, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) show maximum toughness at a degree of crystallinity around 57 %. Probably, toughness is influenced by the combined effects of the very high molar mass [3,27] and the degree of crystallinity. In the non-irradiated PE-UHMW material states these effects result in an optimum degree of crystallinity for high fracture toughness. In the irradiated material states (1020g, 1050g, Dsa, Lsa, X3sa) $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ are on a lower level. In these material states the effects of molar mass and degree of crystallinity is additionally superposed by crosslinks in the amorphous phase (which is in an elastomeric state). These crosslinks influence the structure of the amorphous phase and hence, the crack growth behaviour (see discussion Figure 62-64)

The bimodal LTD in the warm irradiated and remelted hip implant (Dsa) does not affect the fracture toughness compared to monomodal LTD in Lsa. Maybe, the slightly better fracture toughness of X3sa can be attributed to the absence of small fragmented lamellae in these hip implants. This hypothesis has to be further tested.



Figure 57: Correlation of $J_{0.2}$ – technical crack initiation with the degree of crystallinity calculated from the first DSC heating run



Figure 58: Correlation of $dJ/d\Delta a | 0.2$ – measure for stable crack growth with the degree of crystallinity calculated from the first DSC heating run

The probability of occurrence of tie molecules in polyethylene (p) and the tie molecule and entanglement area fraction at the crystal-amorphous interface (F_s) do not correlate with J_{0.2} and dJ/d Δa |_{0.2} (Figure 59 and Figure59). The p- values are very similar in non-irradiated material states (RER, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng). Despite their slight increase in p with increasing molar mass (compare GUR 1020, GUR 1020VitE, 1020ng with RER, GUR 1050, 1050ng) no influence on J_{0.2} and dJ/d Δa |_{0.2} is measurable (Figure 59, left and Figure 59, left). In the irradiated material states (1020g, 1050g, Dsa, Lsa, X3sa) the p-values cover a similar but broader range. Nevertheless, independently form p-values fracture toughness is lower in these material states. Again, this indicates the importance of the properties of the amorphous phase (e.g. crosslinking) on the fracture behavior of PE-UHMW. The concentration of mechanically active species does not influence the fracture process. F_s correlates with the degree of crystallinity (Figure A.4.1-4, see Appendix) and hence, a qualitatively similar dependency of $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ on F_s and degree of crystallinity evolve (only X3sa shows differences: the p-value is very low and the degree of crystallinity is very high resulting in a moderate F_s value).



Figure 59: Correlation of $J_{0.2}$ – technical crack initiation with p - probability of occurrence of tie molecules (left) and F_s – tie molecule and entanglement area fraction at the crystal-amorphous interface (right)



Figure 60: Correlation of $dJ/d\Delta a|_{0.2}$ – measure for stable crack growth with p - probability of occurrence of tie molecules (left) and F_s – tie molecule and entanglement area fraction at the crystal-amorphous interface (right)

Characteristic toughness values do not depend on structural parameters at nano-meter scale. Average lamellar thickness l_c (Figure A.4.1-34 and Figure A.4.1-35, see Appendix), thickness of the amorphous phase l_a (Figure 61), and the long period l_p (Figure A.4.1-36 and Figure A.4.1-37, see Appendix) do not correlate with $J_{0.2}$ and $dJ/d\Delta a |_{0.2}$. Beerbaum [138] found an increase in $J_{0.2}$ (determined by instrumented impact testing) with increasing l_a in PE-HD while $J_{0.2}$ was unaffected by l_p . The thicker the amorphous domains are the more energy and strain can be absorbed, and the more voids are generated during the fracture process in PE-HD.



Figure 61: Correlation of $J_{0,2}$ – technical crack initiation (left) and $dJ/d\Delta a|_{0,2}$ – measure for stable crack growth (right) with l_a – thickness of the amorphous phase

In PE-UHMW the behavior of the material in the process zone is different (see 4.1.6). No cavitation takes place in the amorphous phase of the polymer ahead of the crack tip. Hence, the thickness of the amorphous phase does not directly influence crack initiation and stable crack growth (Figure 61).

In order to evaluate the characteristics of the amorphous phase, the chemical parameters are correlated to the fracture toughness. Baker et al. [18] found a decrease in fatigue crack propagation with increasing irradiation dose. The technical crack initiation does not correlate with the total irradiation dose (in terms of TVI) in the material states tested in this Thesis (1020g, 1050g, Dsa, Lsa, X3sa; Figure 62, left). The influences of thermal treatment on the distribution of amorphous and crystalline phase partially compensate the negative effects of irradiation on crack initiation. Resistance against stable crack growth slightly decreases with increasing total irradiation dose (Figure 62, right). This result shows that the effects off irradiation influence crack initiation and stable crack growth behaviour in a different manner.



Figure 62: Correlation of $J_{0,2}$ – technical crack initiation (left) and $dJ/d\Delta a|_{0,2}$ – measure for stable crack growth (right) with TVI – trans vinylene index

Reduction in the mobility of the melt leads to an increase in temperature at the beginning of crystallization $T_{c,onset}$ which is used as a measure for the mobility of the amorphous phase at ambient temperature too (see 4.1.3). Fracture toughness depends on the mobility of the amorphous phase: $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ decreases with increasing $T_{c,onset}$, i.e. with decreasing mobility of the amorphous phase (Figure 63). This dependencies is stronger for $dJ/d\Delta a|_{0.2}$ than for $J_{0.2}$ Nevertheless, the $T_{c,onset}$ values cannot explain the relatively low fracture toughness of GUR1050.



Figure 63: Correlation of $J_{0,2}$ – technical crack initiation (left) and $dJ/d\Delta a|_{0,2}$ – measure for stable crack growth (right) with $T_{c,onset}$ – temperature at the beginning of crystallization

Crack initiation and stable crack growth are influenced by the concentration of the terminal vinyl group: $J_{0.2}$ and $dJ/d\Delta a|_{0.2}$ decrease with decreasing TermVI (Figure 63). These correlations apply for non-irradiated (RER, GUR 1020, GUR 1020 VitE, GUR 1050, 1020ng, 1050ng) as well as irradiated material states (1020g, 1050g, Dsa, Lsa, X3sa). The reduction in TermVI indicates Y-crosslinking. Fu et al. [74] found an increase in terminal vinyl groups after high temperature melting of PE-UHMW due to massive chain scission. When there is not much chain scission (only slightly higher vinyl index) the impact toughness is sharply increased. Tensile work to failure increased with increasing terminal vinyl index up to a certain extend and decreases then. Obviously, the J determined fracture toughness shows qualitatively similar behavior. The relatively low $J_{0.2}$ value in GUR 1050 corresponds to a low TermVI. The low TermVI probably indicates that temperature during consolidation was lower than in the other non-irradiated PE-UHMW material states. This hypothesis has to be further confirmed with different lots of consolidated PE-UHMW.



Figure 64: Correlation of $J_{0,2}$ – technical crack initiation (left) and $dJ/d\Delta a|_{0,2}$ – measure for stable crack growth (right) with TermVI – terminal vinylene index

As the availability of the amorphous phase (reflected by l_a) alone does not correlate with the toughness, it is combined with the "quality" of the amorphous phase in terms of TermVI: the TermVI is multiplied with the thickness of the amorphous phase l_a (Figure 65). One gets a measure for the concentration of the polymer end group (reflecting the extend of Y-crosslinking and consolidation parameters) and the availability of the amorphous phase during crack growth.



Figure 65: Correlation of $J_{0.2}$ – technical crack initiation (left) and $dJ/d\Delta a|_{0.2}$ – measure for stable crack growth (right) with $T_{c,onset}$ multiplied by l_a (nm); in Dsa the thickness of the amorphous phase is probably overestimated by DSC method (see 3.3.2) - the value is excluded from the correlations

These results show that fracture toughness is highly influenced by the amorphous phase. Optimization of fracture toughness in PE-UHMW for total joint replacement has to focus on this phase preferentially.

4.2 Anisotropy induced during consolidation, physico-chemical treatment and in vivo use

This chapter discusses characteristic values as a function of surface and areas of PE-UHMW implants. The values of the material states are discussed just in 4.

The changes in the material during its life cycle are discussed on the basis of the results from each measurement technique.

4.2.1 Results from FTIR measurements

The characteristic values - oxidation index OI, trans vinylene index TVI, terminal vinylene index TermVI, and the degree of crystallinity - were calculated from the FTIR Spectra in order to present depth profiles (see 3.3.1).

The depth profiles TVI and TermVI show constant values with statistic scattering as a function of distance from surface (the depth profiles show no trend; Figure A.4.2.1-1- A.4.2.1-12, see Appendix). Hence, manufacturing does not result in inhomogeneities concerning TermVI in any material states. The irradiation dose-depth distribution is homogenous in all irradiated material states as indicated by TVI (1020g, 1050g, Dsa, Lsa, X3sa, GAN, FIN, MAS).

The constant values with statistic scattering as a function of distance from surface are measured in OI and the degree of crystallinity for all material states (Figure A.4.2.1-2 – 20, see Appendix) except ram extruded PE-UHMW (RER), gamma-sterilized GUR 1050 (1050g) and the explants GAN, FIN, and MAS. These characteristic values of the later materials states are discussed together with the results from FTIR mapping.

The results of rim and center areas, inner and outer surfaces do not differ substantially for any material states (Figure A.4.2.1-21 – 23, see Appendix), except the explants GAN, FIN, and MAS (see 4.2.1.6). For an overview see Table 8.

Table 8: Overview about the results from FTIR measurements; OI ... oxidation index, TVI ... trans vinylene index, TermVI ... terminal vinyl index, Δ ... differences between center -, rim area, outer or inner surface (applicable only in hip liners), n.a. ... not applicable; a) only first value elevated, b) some higher OI values due to mechano-oxidative degradation (see 4.2.1.3), c) some higher OI values due to thermo-oxidative degradation (see 4.2.1.5), d) biomolecules diffused into the explant during *in vivo* use

	OI		TVI		TermVI		X _{FTIR}	
	depth profile	Δ	depth profile	Δ	depth profile	Δ	depth profile	Δ
CMS	-	n.a.	n.a.	n.a.	-	n.a.	-	n.a.
RER	+	n.a.	n.a.	n.a.	-	n.a.	+	n.a.
GUR 1020	_ ^{a)}	n.a.	n.a.	n.a.	-	n.a.	_ ^{a)}	n.a.
GUR 1020VitE	n.a.	n.a.	n.a.	n.a.	-	n.a.	-	n.a.
GUR 1050	-	n.a.	n.a.	n.a.	-	n.a.	-	n.a.
1020ng	_ ^{b)}	-	n.a.	n.a.	-	-	-	-
1050ng	-	-	n.a.	n.a.	-	-	-	-
1020g	-	-	-	-	-	-	-	-
1050g	+	-	-	-	-	-	-	-
Dsa	-	-	-	-	-	-	-	-
Lsa	- ^{c)}	-	-	-	-	-	-	-
X3sa	-	-	-	-	-	-	-	-
GAN	+ ^{d)}	+	-	-	-	-	-	-
FIN	+	-	-	-	-	-	-	-
MAS	+	+	-	-	-	-	+	+

The results of the FTIR mapping are in Figure A.4.2.1-24 – 51 (see Appendix), selected FTIR mapping profiles are discussed in 4.2.1.1 - 4.2.1.6.

4.2.1.1 Consolidation of PE-UHMW (RER, CMS)

The ram extruded material (RER) revealed maximum values for oxidation index OI at the surface. This value diminishes and reaches after app. 1.26 mm a value of $OI = 0.005 \pm 0.003$ (bulk oxidation). The degree of crystallinity (determined with FTIR) is elevated in the very surface layer compared with bulk material (see Figure 66, data from compression molded sheet CSM included for comparison reason.) These results indicate that ram extrusion damages the outer layers of the material. The shortened chains can crystallize more easily and lead to a higher degree of crystallinity.



Figure 66: FTIR data: comparison of oxidation index (OI) and degree of crystallinity - compression molded sheet (CSM) and ram extruded rod (RER) from surface areas inwards (in the case of RER, from area A and B)

In the ram extruded rod, the normalized FTIR spectra of the surface layers show a peak centered at 1720 cm⁻¹ (Figure 67 and Figure A.4.2.1-24, see Appendix.) The peak is associated with thermo-oxidative degradation [116]. The FTIR spectra from the surface layer do not show a peak centered at 1738 cm⁻¹. This peak is associated with mechano-oxidative degradation [119]. The chemical damage of the polymer during the ram extrusion process is dominated by thermo-oxidative degradation. Thermo-oxidative degradation is highest at the surface. The height of the peak diminishes from the surface inwards. The normalized spectra between 10 and 11 mm (and around 29.5 mm from surface A) show a peak centered at 1738 cm⁻¹. In this case, it originates from sample preparation (i.e. microtoming) presumably [226].



Figure 67: Ram extruded rod RER - FTIR mapping form surface area A inwards: carbonyl region

4.2.1.2 Influence of powder type (GUR 1020, GUR 1020VitE and GUR 1050)

GUR 1020 shows a low OI at the surface and no bulk oxidation index is measurable at a distance from the surface of 0.36 cm (Figure A.4.2.1-2, see Appendix.). At the very surface the carbonyl region in the FTIR spectra of GUR 1020 (Figure 68) shows a peak at 1743 cm⁻¹. This peak cannot be attributed to a specific chemical compound yet. Nevertheless, this peak was measured in other samples of various other material states too (e.g. [227]). In polymer degradation a lot of different chemical species emerge: the oxidative degradation products contain e.g. a keton group, but each keton has polymer chains of different length bound to the C of the C=O group. Hence, the peak resulting from C=O groups in FTIR spectra is broadened compared with the peak of a single chemical species [211]. The mechanisms involved in generating the 1743 cm⁻¹ - peak can be associated with oxidative degradation, since the degree of crystallinity (determined by FTIR) is slightly higher in this sample.

In GUR 1020 VitE no OI can be determined, as can be seen in the FTIR spectra (Figure A.4.2.1-26, see Appendix).

A very low OI at the surface is calculated from the spectra of GUR 1050 and no bulk oxidation index is measurable at a distance from the surface of 2.88 cm (Figure A.4.2.1-2, see Appendix). The carbonyl region of the FTIR spectra from GUR 1050 (Figure 69) shows a wavy base line with small irregularities at 1738 cm⁻¹, 1720 cm⁻¹ and 1704 cm⁻¹. None of these irregularities can be regarded as a peak itself. Empirically, such a wavy baseline in the carbonyl region indicates that oxidative degradation is about to start. This early stage of polymer damage can result form consolidation process or from sample preparation (e.g. microtoming). The degree of crystallinity is not influenced by this low oxidative degradation.



Figure 68: GUR 1020 - FTIR mapping: carbonyl region



Figure 69: GUR 1050 - FTIR mapping: carbonyl region

4.2.1.3 Manufacturing – milling and cleaning of implants (1020ng, 1050ng)

The OI is very low and shows a constant value with statistic scattering in1020ng, except three values in the depth profiles of OI from 1020ng center inner surface and outer surface (Figure A.4.2.1-3, see Appendix) app. 1 mm below the surface. Figure 70 shows a peak at 1738 cm⁻¹ in a spectrum of 1020ng approximately 1 mm below the surface (resulting in the higher OI value in the depths profiles). This peak is associated with mechanical degradation of the polymer.

Since no oxidative degradation is measurable on the surface of the virgin implant, this peak originates from the microtoming step presumably. The influence of microtoming on the degradation of the polymer was investigated by Bracco et al. [226] and they found oxidation in this sample preparation step. Hence, the sample preparation has to be done with care. Especially at low oxidative degradation state of the material it influences OI enormously and the reason for an unexpected high OI in a depth profile should always be elucidated by evaluation of the corresponding normalized spectrum.



Figure 70: Virgin implant, GUR 1020, non gamma-sterilized (1020ng) - FTIR mapping center inner surface: carbonyl region

4.2.1.4 Gamma-sterilization under nitrogen atmosphere (1020g, 1050g)

The depth profiles of OI for 1050g show slightly higher values at the surface declining with distance from surface. FTIR mapping will cast further light on this result: The carbonyl region of the normalized FTIR spectra shows a small peak at 1720 cm⁻¹ throughout the depth profile (Figure 71 and Figure A.4.2.1-38 - 40, see Appendix). The peak at 1720 cm⁻¹ is associated with thermo-oxidative polymer degradation [116]. This peak can result from oxidation during irradiation (e.g. if the package would have a leakage) or, more likely, from oxidation after opening the package. The gamma-sterilized samples were exposed to air during sample preparation, storage after sample preparation, and the FTIR measurements. This exposure time was kept as short as possible. Nevertheless, it caused low oxidative degradation in the material already.



Figure 71: Virgin implant, GUR 1050, gamma-sterilized (1050g) - FTIR mapping rim inner surface: carbonyl region

4.2.1.5 Crosslinked PE-UHMW implants – influence of thermal treatment (Dsa, Lsa, X3sa)

The normalized spectra of the virgin implant made from LongevityTM (Lsa) show a rippled baseline and occasionally small peaks centered around 1720 cm⁻¹ and 1738 cm⁻¹ in the spectra (Figure 72 and Figures A.4.2.1-45 - 47, see Appendix). These peaks result in the slightly higher OI values in the depth profiles (Figure A.4.2.1-8, see Appendix). Surprisingly the spectra show oxidative degradation appearing isolated in the depth profiles (no in- or declining values before and afterwards). Normally, isolated oxidation can be attributed to mechano-oxidative degradation i.e. a peak at 1738 cm⁻¹. However, the high values at 1720 cm⁻¹ indicate that this is not the only reason for the peaks and some thermo-oxidative degradation occurred. The reason for these spots of degraded material has to be further elucidated.

The normalized spectra of a virgin implant made from $X3^{TM}$ (X3sa) show a peak centered at 1720 cm⁻¹ (Figure 73 and Figures A.4.2.1-48 - 50, see Appendix). The oxidative degradation is constant in the depth profile of X3sa. Oxidative degradation depth profiles of irradiation-sterilized PE-UHMW implants show a maximum of oxidative degradation at around 1 – 2 mm below the surface after long time exposure to oxygen (see 2.3 and 4.2.1.6). The reason for the behavior of X3sa is uncertain yet, but it is observed in an implant made from X3 (FIN) after *in vivo* use too (see 4.2.1.6).

The peak at 1720 cm⁻¹ can result from thermo-oxidative degradation during irradiation, subsequent thermal treatment and/or shelf aging in gas permeable packaging. It is known from literature that irradiated and annealed PE-UHMW contains remaining radicals. They can cause oxidative degradation when exposed to oxygen instantly. Therefore, the X3sa material state was kept under vacuum to prevent oxidation during the period between opening and measuring. Nevertheless, oxidation during sample manipulation and measurements cannot be precluded.



Figure 72: Virgin implant, LongevityTM (Lsa) - FTIR mapping center outer surface: carbonyl region



Figure 73: Virgin implant, X3 (X3sa) - FTIR mapping center inner surface: carbonyl region

4.2.1.6 Influence of *in vivo* use on irradiation-sterilized and crosslinked PE-UHMW explants (GAN, FIN, MAS)

The depth profiles of OI in the Durasul® (GAN) explant have maximum values at 0.4 - 0.8 mm below the inner surfaces and directly at the outer surface. Below 1.7 mm from inner surface and 0.9 mm from the outer surface the OI declines to 0.003 ± 0.003 and stays constant



Figure 74: FTIR data: comparison of oxidation index (OI, left) and the degree of crystallinity calculated from the FTIR spectra (X_{FTIR} , right) for *in vivo* used explant made from Durasul® (GAN), center unloaded, center loaded, and rim areas from inner (IO) and outer (AO) surface inwards

The OI in the depth profiles is mainly attributed to the 1738 cm⁻¹ band in the FTIR spectra (Figure 75 and Figure 76). This band can be attributed to the ester group resulting from mechano-oxidative degradation or to the ester group of biomolecules [106]. Mechano-oxidative degradation involves chain scission. This leads to recrystallization and hence an elevated degree of crystallinity (see 4.2.1 and 4.2.4). Constant values of the degree of crystallinity (determined by FTIR and DSC) with statistic scattering were measured throughout the depth profiles of the explant GAN (

Figure 74). Hence, the peak at 1738 cm⁻¹ can be attributed to the ester group of biomolecules diffused into the polymer. The contribution of the 1720 cm⁻¹ band, attributed to thermo-oxidative degradation, is very low (0.003 \pm 0.003). The depth profiles of OI reflect diffusion profiles of biomolecules during *in vivo* use. Similar results were published in [106].

The concentration of biomolecules (semi-quantified by OI) is lower in the depth profiles from outer surface than from inner surface inwards. Since diffusion is determined by availability of biomolecules, it can be concluded that the concentration of biomolecules and hence, the contact to the synovial liquid, is lower at outer surfaces than at inner surfaces in Alloclasic endoprosthesis design.

No differences in diffusion profiles were found between loaded and unloaded areas in the GAN explant. This indicates that the loaded area had as much contact with the synovial liquid as the unloaded areas. The outer surface of the rim area has a slightly higher concentration of biomolecules than the outer surfaces of the center areas, indicating more contact with the synovial liquid in the outer rim area (in Alloclasic design).



Figure 75: *In vivo* used explant made from Durasul® (GAN) - FTIR mapping rim outer surface: carbonyl region



Figure 76: In vivo used explant made from Durasul® (GAN) - FTIR mapping rim inner surface: carbonyl region

The depth profiles of OI in the X3 explant (FIN) have maximum values in the surface layers below the inner and the outer surfaces. Below app. 1 mm from the surfaces the OI declines to 0.078 ± 0.007 and stays constant (Figure 77).



Figure 77: FTIR data: comparison of oxidation index (OI, left) and the degree of crystallinity calculated from the FTIR spectra (X_{FTIR} , right) for *in vivo* used explant made from X3 (FIN), center loaded, and rim areas from inner (IO) and outer (AO) surface inwards



Figure 78: In vivo used explant made from X3 (FIN) - FTIR mapping rim inner surface: carbonyl region

The OI in the depth profiles of *in vivo* used explant FIN results from peaks at 1738 cm⁻¹ and 1720 cm⁻¹ (Figure 78 and Figure A.4.2.1-51, see Appendix). The depth profiles of the degree of crystallinity determined by FTIR (and DSC, see 4.2.2.2) show constant values and statistic scattering as a function of distance from surface (Figure 77, right). Hence, the higher peaks at 1738 cm⁻¹ at the surface layers can be attributed to the ester group of biomolecules diffused into the polymer again. The depth profiles of OI reflect not only diffusion profiles of biomolecules during *in vivo* use but also homogenous oxidative degradation. The contribution of the 1720 cm⁻¹ band (attributed to thermo-oxidative degradation) to the OI is higher in FIN (0.078 \pm 0.007 bulk oxidation) than in GAN (0.003 \pm 0.003 bulk oxidation).

The diffusion profiles from outer and from inner surface inwards are similar (in the rim area.) This indicates that the concentration of biomolecules and contact with the synovial liquid is similar during *in vivo* use at inner and outer surfaces in Hipstar endoprosthesis design.

The depth profiles of OI in the radiation-sterilized PE-UHMW explant (MAS) have maximum values at 1.8 mm below the inner surface and directly at the outer surface. Approximately 4 mm below inner surface and 0.9 mm below the outer surface the OI declines to 0.025 ± 0.006 and stays constant (bulk oxidation, Figure 79).



Figure 79: FTIR data: comparison of oxidation index (OI, left) and the degree of crystallinity calculated from the FTIR spectra (X_{FTIR} , right) for *in vivo* used explant made from irradiation sterilized PE-UHMW (MAS), rim area from inner (IO) and outer (AO) surface inwards

The OI in the depth profile of the rim area, inner surface inwards, is mainly attributed to the 1720 cm⁻¹ band in the FTIR spectra (Figure 80), although a proportionally high value at 1738 cm⁻¹ is measured in the surface layers. This indicates heavy thermo-mechanical degradation in the liner and biomolecules which diffused into the surface layers.



Figure 80: *In vivo* used explant made from irradiation sterilized PE-UHMW (MAS) - FTIR mapping rim inner surface: carbonyl region (note different scale of the y-axis)

Heavy chain scission resulted in recrystallization during *in vivo* use and higher degree of crystallinity in the region of high OI (Figure 79). The inner surface exhibits the characteristic oxidative degradation profile reported (see 2.4.1): a maximum OI app. 1 - 2 mm below the

surface can be found in irradiation-sterilized PE-UHME exposed to oxygen for a longer period of time. The maximum OI values in MAS are very high, around 2.5 (at OI > 3 all mechanical integrity of PE-UHMW is lost [28]).

FTIR mapping of the outer surface inwards revealed a peak at 1738 cm⁻¹ in the first three spectra and a small peak at 1720 cm⁻¹ throughout the profile in the rim area (Figure 81). The shoulder at 1697 cm⁻¹ cannot be attributed to a specific chemical group yet. The depth profile from outer surface inwards does not show the reported behavior. Instead, there is low but homogenous oxidative degradation and constant degree of crystallinity throughout the profile (Figure 79). This behavior may be associated with the limited contact with the oxygen in the synovial liquid at the backside of the Alloclasic prosthesis design (compare with diffusion of biomolecules in explant GAN, discussed previously).



Figure 81: *In vivo* used explant made from irradiation sterilized PE-UHMW (MAS) - FTIR mapping rim outer surface: carbonyl region

4.2.2 Results from DSC experiments

The characteristic values – the melting point in the first and second heating run, the crystallization temperature, the temperature at the beginning of the crystallization, and the degree of crystallinity calculated from the first and the second heating run - were calculated from the DSC data in order to present depth profiles (see 3.3.2). Generally, differences in characteristic values should not be interpreted if they are less than 1 °C (temperatures) or less than 2 % (degree of crystallinity) due to limitations of the DSC method itself.

The depth profiles of the characteristic temperatures and the degree of crystallinity show constant values with statistic scattering as a function form distance from surface (the depth profiles show no trend; Figure A.4.2.2-1 - 46, see Appendix).

Only in ram extruded PE-UHMW and in the explant MAS morphological inhomogeneities are measured. They are discussed together with the lamellar thickness distribution in 4.2.2.1 and 4.2.2.2. Obviously, the adsorption of biomolecules does not affect the morphology in terms of degree of crystallinity and LTD in the highly crosslinked explants (GAN and FIN).

The results from rim and center areas, inner and outer surfaces do not differ for all material states (A.4.2.2-47 – 62, see Appendix).

An overview about the results from DSC measurements is given in Table 9.

Table 9: Overview about the results from DSC measurements; T_{m1} ... melting point in the first heating run, T_{m2} ... melting point in the second heating run, T_c ... crystallization temperature, $T_{c, onset}$... temperature at the beginning of the crystallization, Δ ... differences between center and rim or outer and inner surface (applicable only by investigations of hip liners), n.a. ... not applicable; a) differences within the precision of the method, b) only first value elevated;

	T _{m1}		T _{m2}		T _c		T _{c,onset}		X _{DSC,1}		X _{DSC,2}	
	depth profile	Δ	depth profile	Δ	depth profile	Δ	depth profile	Δ	depth profile	Δ	depth profile	Δ
CMS	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.
RER	+	n.a.	_ ^{a)}	n.a.	+	n.a.	+	n.a.	+	n.a.	+	n.a.
GUR 1020	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.
GUR 1020VitE	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.
GUR 1050	-	n.a.	-	n.a.	-	n.a.	-	n.a.	_b)	n.a.	_ ^{b)}	n.a.
1020ng	-	-	-	-	-	-	-	-	-	_ ^{a)}	-	_ ^{a)}
1050ng	-	-	-	-	-	-	-	-	-	-	-	-
1020g	-	-	-	-	-	-	-	-	-	-	-	-
1050g	-	-	-	-	-	-	-	-	-	-	-	-
Dsa	-	-	-	-	-	-	-	-	-	-	-	-
Lsa	-	-	-	-	-	-	-	-	-	-	-	-
X3sa	-	-	-	-	-	-	-	-	-	-	-	-
GAN	-	-	-	-	-	-	-	-	-	-	-	-
FIN	-	-	-	-	-	-	-	-	-	-	-	-
MAS	-	-	-	-	-	-	-	-	+	-	+	-

The lamellar thickness distribution (LTD) is calculated from the first and the second heating run according to equation 32 (Figure A.4.2.2-63 -95, see Appendix). No variations within the depth profiles and the different areas in implants are observed, except in ram extruded material (RER) and the irradiation sterilized explant (MAS).

4.2.2.1 Consolidation of PE-UHMW (RER, CMS)

The characteristic values for ram extruded PE-UHMW are shown in Figure 82 and Figure 83. In the ram extruded samples the melting temperature in the first heating run T_{m1} is significantly elevated in the surface layer compared to bulk layers. This effect will be further discussed together with the evaluation of the LTD. The melting temperature in the second heating run T_{m2} is within a 1 °C range in the whole depth profile (differences cannot be interpreted meaningfully). The crystallization temperature T_c , and the temperature at the beginning of the crystallization $T_{c, onset}$ are significantly lower in the surface layers down to a depth of 0.90 mm. The lower temperatures at the beginning of the crystallization and at its maximum indicate a different crystallization behavior: Oxidative degradation reduces the molar mass of the PE-UHMW. This reduction enhances the mobility of the polymer chains in the melt (see 4.1.3).



Figure 82: Ram extruded rod RER – DSC data from surface area B inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the minimum temperature during crystallization (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$; surface area B - similar values for surface area A, Figure A.4.2.2-2, see Appendix;

The degree of crystallinity in the ram extruded rod (Figure 83) is significantly elevated in the first heating run (down to a depth of 0.54 mm) and in the second heating run (down to a depth of minimum 0.90 mm). The results calculated from the first heating run indicate recrystallization of the degraded polymer during the ram extrusion process. The higher degree of crystallinity calculated from the second heating run reflects the reduction in molar mass (chemical changes in the polymer) and cannot be attributed to thermal or mechanical history of the sample.



Figure 83: Ram extruded rod RER - DSC data: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run; surface area B - similar values for surface area A, Figure A.4.2.2-25, see Appendix;

The lamellar thickness distribution (LTD) gives a more detailed picture of the PE-UHMW morphology. The LTDs were calculated from the first and the second heating runs and the results shown in Figure 84. The LTD of the ram extruded rod shows a different distribution for surface and bulk layers. In the first heating run the LTD of the surface layers have a maximum at app. 23 nm and the central layers have a maximum at app. 21 nm (Figure 84). This indicates that the crystallization during the consolidation process leads to slightly thickened lamellae in the surface layers. These slightly thickened lamellae are pictured in the higher melting temperature in the first heating run. In the second heating run the maximum is shifted to app 16 nm in the surface layers and to app. 18 nm in the bulk layers. The shift in LTD is

attributed to the different nucleation and crystallization behavior in the degraded surface layers.



Figure 84: Ram extruded rod RER - Lamellar thickness distribution calculated from the first (above left) and second (above right) heating run

4.2.2.2 Influence of in vivo use on irradiation-sterilized and crosslinked PE-UHMW explants (GAN, FIN, MAS)

The explant made from irradiation-sterilized PE-UHMW (MAS) shows a higher degree of crystallinity in the highly oxidized region compared with the surface and bulk material (Figure 85). This result is qualitatively similar to the results calculated from FTIR data. In order to account for the variations in the depth profile of MAS two material states were separated: MAS, oxidized, and MAS, bulk material.



Figure 85: In vivo used explant made from irradiation sterilized PE-UHMW (MAS), rim – DSC data from inner surface area inwards: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run

The lamellar thickness distributions calculated from the first heating run of the irradiation sterilized PE-UHMW explant (MAS) show little differences in the height of the maxima (Figure 86). This indicates lamellar thickening due to recrystallization *in vivo*. The peak in LTD calculated from the second heating run of oxidized material is shifted to higher values compared with bulk material (Figure 86).



Figure 86: *In vivo* used explant made from irradiation sterilized PE-UHMW (MAS), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first heating run (left) and the second heating run (right)

Probably due to the severe oxidation the polymer chains are degraded that much, that entanglements in the melt do not hinder reptation to the extent of chains in virgin material and slightly oxidized PE-UHMW. Tight folding of a single polymer chain during crystallization is facilitated and thicker lamellae emerge (compare with RER, see 4.2.1.2).

4.2.3 Results from DSI tests

In implants depth profiles of H_{IT} and E_{IT} were recorded in reduced number, since the investigations on the chemical structures and the physical morphology revealed no differences between center and rim areas, inner and outer surfaces. The areas and surfaces which were investigated are given in Tables A,4.2.3-1 – 4, see Appendix.

In all material states except ram extruded PE-UHMW (RER), explant GAN, and explant MAS the depth profiles of microhardness (H_{IT}) and indentation modulus (E_{IT}) show constant values with statistic scattering as a function form distance from surface (the depth profiles show no trend, Figures A.4.2.3-1 – 8, see Appendix).

Only in explant GAN, inner and outer surface show different micro mechanical properties (see 4.2.3.2). No substantial differences were measured in the center and rim areas of the other material states (Figure A.4.2.3-9 and Figure A.4.2.3-10, see Appendix).

An overview about the result from DSI testing is given in Table 10.

Table 10: Overview about the results from DSI measurements; H_{IT} ... micro hardness, E_{IT} ... indentation modulus, Δ ... differences between center and rim or outer and inner surface (applicable only by investigations of hip liners), n.a. ... not applicable; a) differences within the precision of the method, b) only first value elevated; a) not as clear as for indentation modulus

	Н	п	E _{IT}		
	depth profile	Δ	depth profile	Δ	
CMS	-	n.a.	-	n.a.	
RER	+	n.a.	+	n.a.	
GUR 1020	-	n.a.	-	n.a.	
GUR 1020VitE	-	n.a.	-	n.a.	
GUR 1050	-	n.a.	-	n.a.	
1020ng	-	-	-	-	
1050ng	-	-	-	-	
1020g	-	-	-	-	
1050g	-	-	-	-	
Dsa	-	-	-	-	
Lsa	-	-	-	-	
X3sa	-	-	-	-	
GAN	+ ^{a)}	+ ^{a)}	+	+	
FIN	-	-	-	-	
MAS	+	n.a.	+	n.a.	

4.2.3.1 Consolidation of PE-UHMW (RER, CMS)

Figure 87 shows the depth profiles of hardness H_{IT} and indentation moduli E_{IT} for ram extruded rod (RER) and compression molded sheet (CMS, for comparison reasons). The tests were performed on Hysitron Triboindenter® (see 3.4.1).

In the compression molded sheet the homogenous chemical and physical structure results in homogenous mechanical properties on micro-meter scale throughout the compression molded PE-UHMW.

The depth profiles of the ram extruded rod show elevated values in the surface layers for hardness H_{IT} and for indentation modulus E_{IT} (see Figure 87). These results indicate that the chemical and morphological changes influence the micro-mechanical properties: oxidative degradation leads to an elevated degree of crystallinity. This increase results in higher values of micro-hardness and indentation modulus in the surface layers up to a distance of app. 1 mm from surface.



Figure 87: Compression molded sheet CMS and ram extruded rod RER – comparison of micro hardness H_{IT} as a function from the distance from surface (left) of indentation modulus E_{IT} as a function from the distance from surface (right)

4.2.3.2 Influence of *in vivo* use on irradiation-sterilized and crosslinked PE-UHMW explants (GAN, FIN, MAS)

The depth profiles from all areas and surfaces of the explant made from Durasul® (GAN) are shown in Figure A.4.2.3-7 and Figure A.4.2.3-8, see Appendix. The explant GAN shows reduced values of indentation modulus in the regions up to app. 1 mm below the inner surfaces (Figure 88, right). No reduction in indentation modulus is observed at the outer surface. The depth profiles of micro-hardness do not clearly exhibit reduced values below any surface (Figure 88, left).



Figure 88: *In vivo* used explant made from Durasul® (GAN) – comparison of micro hardness (left) and indentation modulus (right) as a function from the distance from surface

Costa et al. [106] postulated a plasticizer effect of biomolecules diffused into PE-UHMW prosthetic components during *in vivo* use. Greenbaum et al. [107] showed that molecules of biological origin (squalene and cholesterol) adversely affect the compression properties in PE-UHMW *in vitro*. If the results from DSI testing are compared with the results from FTIR mapping (Figure 89), it is obvious that in the regions of high concentrations of biomolecules (i.e. below inner surfaces) the modulus is reduced.



Figure 89: In vivo used explant made from Durasul® (GAN) – comparison of indentation modulus (E_{IT}) and the concentration of ester groups (c_{ester} , a quantitative measure for the diffusion of biomolecules into the hip liner) as a function from the distance from surface

Hence, the plasticizer effect of biomolecules, postulated previously, is proved in explant GAN (degree of crystallinity is constant throughout the depth profile,

Figure 74). Probably, the plastic material behavior contributing to the micro-hardness is less sensitive to plasticizing. Hence, the mirco-hardness is not significantly reduced at the surface layers.

The depth profiles of the explant made from X3 (FIN) does not show reduced values at the surface for micro-hardness and indentation modulus (Figure 90). Biomolecules are analyzed in the surface areas of this explant too, but their concentration is lower than in GAN. This, together with higher bulk oxidation in FIN, might be the reason that no plasticizer effect is measurable.



Figure 90: *In vivo* used explant made from X3 (FIN) – comparison of micro-hardness (left) and indentation modulus (right) as a function from the distance from surface

The depth profiles of micro-hardness and indentation modulus of the irradiation sterilized explant (MAS) show very high values app. 1.5 mm below the surface. In this area the degree of crystallinity is elevated due to recrystallization of highly oxidized PE-UHMW. Similar results were found in other explants made from irradiation sterilized PE-UHMW [165,223]. The plasticizer effect of biomolecules diffused into the explant cannot be evaluated in MAS, since it is superposed with the adverse effect of the increase of crystallinity due to oxidative degradation.



Figure 91: *In vivo* used explant made from irradiation sterilized PE-UHMW (MAS) – comparison of micro-hardness (left) and indentation modulus (right) as a function from the distance from surface

5 Conclusion

This thesis correlates structural parameters with mechanical properties of PE-UHMW used in total hip joint replacement and investigates anisotropy induced during life cycle of the hip components on micro-meter scale. The chemical architecture of the PE-UHMW is analyzed comprehensively by Fourier transformed infra red spectroscopy (FTIR). The morphology and structural parameters at nano-meter scale are investigated by differential scanning Calorimetry (DSC) measurements. The results from these methods are correlated to micro-mechanical properties determined by depth sensing indentation technique. A test method based on the fracture mechanical J-integral concept is established in order to test the fracture behavior of PE-UHMW on component level. The influence of structural parameters on the fracture properties evaluated by this method is discussed.

The material states in this these cover the life cycle of PE-UHMW hip liners (acronyms are grey):

- consolidation method (ram extrusion and compression molding; RER, CMS),
- different molar mass (GUR 1020 and GUR 1050),
- additivation by vitamin E (GUR 1020 containing 0.1 %wt vitamin E; GUR 1020VitE),
- manufacturing (virgin liners milled from GUR 1020 and GUR 1050 stock material and cleaned; 1020ng, 1050ng),
- gamma-sterilization under inert atmosphere (virgin liners; 1020g, 1050g),
- crosslinked PE-UHMW (effects of temperature during irradiation and subsequent thermal stabilization by remelting and annealing are evaluated by investigating virgin liners made from Durasul®, LongevityTM and X3TM; Dsa, Lsa, X3sa)
- *in vivo* use (the effects are exemplarily discussed for explants made from Durasul® GAN, X3TM FIN, and radiation sterilized PE-UHMW MAS)

The results show that the manufacturing process of PE-UHMW hip implants influences their structure and properties. Different from what might be expected from these processes, anisotropy is induced during consolidation step only. Structural and mechanical anisotropy is essentially developing during *in vivo* use. Nevertheless, it is founded in the manufacturing processes, e.g. gamma-sterilization or cross linking procedures.

Consolidation method (RER, CMS), molar mass (GUR 1020, GUR 1050), and additivation by vitamin E (GUR 1020VitE) do not influence bulk oxidative degradation which is very low to zero in these material states. In ram extruded PE-UHMW (RER) the outer layer (up to app. 1.3 mm below the surface) is affected by thermo-oxidative degradation. The damaged layers have been milled away during manufacturing of the hip implant as no anisotropy in oxidative degradation is measurable (1020ng, 1050ng). Gamma-sterilization of hip implants (1020g, 1050g) leads to an increase in oxidative degradation (probably after opening the packages, during sample preparation and measurements), which is still low and homogenous. After in vivo use severe oxidation is found in an irradiation sterilized hip explant (MAS). A maximum of oxidative degradation is measured 1.8 mm below the surface which has been in contact with the synovial liquid. The free macroradicals generated in the material have not been quenched after irradiation by any thermal treatment (and the material is not stabilized by any additive). Hence, the degradation maximum evolves from diffusion of products from the irradiation treatment and oxygen from the synovial liquid in the material. Radiation-cross linked and remolded PE-UHMW (Dsa, Lsa) show a wavy baseline in the carbonyl region of the normalized FTIR spectra. This indicates empirically that oxidative degradation is about to begin (semi-quantification in terms of oxidation index OI show similar values as non-irradiated implants – 1020ng, 1050ng). Radiation crosslinked and annealed PE-UHMW (X3sa) shows oxidative degradation and highest OI of the virgin material states (1020ng, 1050ng, 1020g, 1050g, Dsa, Lsa). The OI is further increased in the explant made from X3TM (FIN) whereas the OI is not increased in the explant made from Durasul® (GAN). Obviously, the remelting stabilizes PE-UHMW better against oxidative degradation than annealing does. All *in vivo* used explants (GAN, FIN, MAS) show evidence of biomolecules diffused from the synovial fluid into the PE-UHMW surface layers.

Besides oxidative degradation, the concentration of terminal vinvl groups (in terms of TermVI) and trans vinylene groups (in terms of TVI) is semi-quantified from the FTIR spectra. TermVI is affected by consolidation (indicating chain scissioning) and by irradiation, (indicating Ycrosslinking). The temperature during consolidation causes slight scission of the polymer chains (TermVI is increased). This enhances chain diffusion across the particle boundaries and cohesion of the particles. Hence, the TermVI is a potentially powerful structural parameter which characterizes the quality of the consolidation process. In GUR 1050, the TermVI is lower than in the other consolidated material states (RER, CMS, GUR 1020, GUR 1020VitE, 1020ng, 1050ng). In the crosslinking process terminal vinyl groups are consumed (TermVI is reduced) as Y-crosslinks form. The TVI is a measure for total irradiation dose. The dose-depth distributions are homogenous in all irradiated material states (1020g, 1050g, Dsa, Lsa, X3sa, GAN, FIN, MAS). TVI is higher in crosslinked PE-UHMW (Dsa, Lsa, X3sa, GAN, FIN) than in irradiation-sterilized implants (1020g, 1050g, MAS). The TermVI and TVI differ in the crosslinked PE-UHMW hip implants UHMW (Dsa, Lsa, X3sa, GAN, FIN), although the total irradiation dose is similar in these material states (90 - 100 kGy). Apparently, temperature during irradiation and the crosslinking processes influence the concentrations of terminal vinyl- and trans vinylene groups. The mechanisms have to be further elucidated.

Consolidation method (RER, CMS) does not influence the degree of crystallinity and the average lamellar thickness (determined by DSC). The degree of crystallinity is influenced by molar mass: GUR 1050 shows a lower degree of crystallinity than GUR 1020. Gammasterilization (1020g, 1050g) leads to an increase in degree of crystallinity and thickening of the lamellae due to release and recrystallization of scissioned polymer chains. The effect of higher initial molar mass is still measurable: the degree of crystallinity is lower in 1050g than in 1020g. The degree of crystallinity is influenced by thermal treatment after irradiation, not primary by total irradiation dose (or initial molar mass) in crosslinked PE-UHMW. Crosslinking and remelting reduces the degree of crystallinity: the free radicals form chemical bonds in the melt. These crosslinks cannot be incorporated in the crystalline phase during crystallization. Therefor, the degree of crystallinity is lower in Durasul® (Dsa, GAN) and LongevityTM (Lsa) than in non-irradiated material states (e.g. GUR 1020, GUR 1050). Crosslinking and annealing results in a higher degree of crystallinity: again, the cross links are formed in the amorphous phase. During the annealing step unmodified sections of the polymer chain attach to the crystallites due to higher chain mobility at elevated annealing temperature. Ergo, the degree of crystallinity is higher in X3TM (X3sa, FIN) than in non-irradiated material states (e.g. GUR 1020, GUR 1050). Oxidative degradation of the polymer chains leads to recrystallization of the shortened chains. The degree of crystallinity increases linearly with increasing OI. As a result, the crystallinity is elevated in outer layer of ram extruded PE-UHMW (RER; up to app. 0.9 mm below the surface) and in the region up to 4 mm below the surface in the irradiation-sterilized explant (MAS). In vivo use did not influence bulk crystallinity in the investigated explants (GAN, FIN, MAS) compared with virgin hip implants made from the same material (Dsa, Lsa, 1020g, 1050g).

Preordered domains exist in PE-UHMW melt due to the very high molar mass. These domains act as nuclei during crystallization. They dissolve worse in crosslinked PE-UHMW as the crosslinking reduces the mobility of the polymer chains. The crystallization starts at lower degree of super-cooling (at higher temperature in the DSC experiments). In contrast, lower molar mass leads to enhanced mobility of the polymer chains in the melt. A higher degree of super-cooling (lower temperature in the DSC experiments) is necessary to start crystallization. Hence, the temperature at the beginning of the crystallization ($T_{c, onset}$) is a sensitive parameter which reflects changes in the chain mobility in the polymer melt. The interacting forces between the chains in the polymer melt and the amorphous phase above the glass transition temperature are similar in nature. Therefore, $T_{c, onset}$ gives a measure for the mobility of PE-UHMW chains at room temperature too. $T_{c, onset}$ is highest in the crosslinked PE-UHMW

material states (Dsa, LSa, X3sa, GAN, FIN) and lowest the non-irradiated material states (RER, CMS, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng). In between crosslinked and non-irradated PE-UHMW is the $T_{c, onset}$ of the gamma-irradiated material states (1020g, 1050g). This reflects that crosslinking occurs during irradiation under inert atmosphere (as well as chain scission – see degree of crystallinity).

The lamellar thickness distribution (LTD) revealed no substantial influence of consolidation method (RER, CMS), molar mass (GUR 1020, GUR 1050), additivation by vitamin E (GUR 1020VitE) or manufacturing (1020ng, 1050ng) on the bulk morphology of PE-UHMW. The damaged surface layers of ram extruded PE-UHMW (RER) show a LTD shifted to slightly higher lamellar thickness (calculated from the first heating run) due to recrystallization. The changed crystallization behavior of the shortened polymer chains leads to a LTD shifted to slightly lower lamellar thickness (calculated from the second heating run). During gammairradiation not only existing lamellae thicken but also a population of small lamellae (app. 10 -15 nm) is generated additionally. This morphology can be related to chain scission during the irradiation process (the changes in crystallization behavior indicated crosslinking too - see above). The LTD reflects the processes during irradiation and thermal treatment conveniently: Durasul® (Dsa, GAN) shows a bimodal LTD with higher fractions of small and bigger lamellae compared with non-irradiated PE-UHMW (e.g. GUR 1020, GUR 1050). During irradiation at 120 °C and remelting crosslinks are generated. They cannot be incorporated in the crystalline lamellae. Upon crystallization this bimodal LTD is locked in by the chemical crosslinks. In LongeviyTM (Lsa) irradiation at 40 °C and subsequent remelting result in a very broad LTD. It is locked in too. The sequential irradiation and annealing processes in X3TM (X3sa, FIN) result in a LDT exhibiting many thick lamellae (33 - 70 nm) and only few thin lamellae (15 - 20 nm). This morphology results from the annealing step – it is not locked in by the chemical structure, as the LTD calculated from the second heating run shows (thick lamellae fraction are remarkably reduced). In vivo use does not influence the LTD substantially in Durasul® (GAN), X3TM (FIN). Neither does it influence radiation sterilized PE-UHMW (MAS).

Load transfer in semicrystalline polymers is governed by concentration of tie molecules and entanglements. Information on the concentration of these mechanically active molecular species is calculated from DSC data. In PE-UHMW the probability of occurrence of tie molecules is very high compared with PE-HD. It reaches a plateau in ultra high molar mass region of PE (molar mass > 1×10^6 g/mol). The differences in molar mass (due to synthesis or crosslinking) and the small differences in the morphology (at comparable thermal crystallization conditions) compensate each other. Since the probability of occurrence of tie molecules is relatively constant in PE-UHMW, tie molecule and entanglement area fraction at the crystal-amorphous interface (F_s) are governed by the degree of crystallinity. F_s values are very high, suggesting that more than 50 % of the polymer chains leave the lamellae and form tie molecules. They do not fold tight and crystallize at an adjacent or nearby site in the crystal.

The micromechanical properties can be correlated to the degree of crystallinity: increase in crystallinity leads to an increase in micro-hardness H_{IT} and indentation modulus E_{IT} . They are indirectly influenced by molar mass, as molar mass influences the degree of crystallinity. The polymer degradation in the surface layer of ram extruded PE-UHMW (RER) and in the oxidized region of the gamma-sterilized explant (MAS) results in mechanical anisotropy: the shortened polymer chains recrystallize, the degree of crystallinity is elevated; hence, H_{IT} and E_{IT} are elevated in these areas too. The average lamellar thickness l_c , like the other structural parameters at nanometer scale, does not influence the micromechanical properties. However, small lamellae resulting from irradiation adversely affect H_{IT} and E_{IT} . A plasticizer effect of biomolecules diffused into the polymer during *in vivo* use, previously hypothesized in literature, is proven: The explant made from Durasul® (GAN) shows reduced micro-hardness and indentation modulus in the areas where biomolecules are analyzed. The plasticizer effect is
superposed by oxidative degradation in the explants made from irradiation-sterilized PE-UHMW (MAS) and $X3^{TM}$ (FIN).

A new fracture toughness testing method based on the J-integral concept is evaluated. Arc shaped specimens allow evaluation of the fracture toughness of PE-UHMW implants on component level. The results qualitatively reflect the fracture toughness of the material states (RER, GUR 1020, GUR 1020VitE, GUR 1050) in comparison with data from impact tests. For the first time a test method makes it possible to monitor the toughness of stock material and implants throughout the whole manufacturing process.

The fracture behavior (in terms of J-R curves) of PE-UHMW is not influenced by consolation method, molar mass (GUR 1020, GUR 1050), additivation by vitamin E (GUR 1020VitE), and manufacturing (1020g, 1050g) and crosslinking (Dsa, Lsa, X3sa). Furthermore, the thermal treatment after irradiation influences the fracture behavior: The fracture toughness is higher in crosslinked and annealed hip implants than in crosslinked and remelted implants. The temperature at irradiation does not influence fracture toughness. Fractography shows no cavitation in front of the crack tip. The material stretches till it fails. A characteristic diamond pattern occurs at the fracture surface of the non-irradiated material states (RER, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng). This pattern is not visible in gamma-sterilized material states (1020g, 1050g) and it is more coarsely textured in crosslinked PE-UHMW (Dsa, Lsa, X3sa). This indicates a different plastic deformation behavior in irradiated PE-UHMW.

Characteristic fracture toughness values are the technical crack initiation $J_{0,2}$ and the derivative of the J-R curve at crack extension 0.2 mm – $dJ/d\Delta a \mid_{0.2}$ (as a measure for stable crack growth). They do not correlate with the degree of crystallinity. The optimum degree of crystallinity for maximum toughness is around 56 % in non-irradiated PE-UHMW (RER, GUR 1020, GUR 1020VitE, GUR 1050, 1020ng, 1050ng) due to combined effects of molar mass and degree of crystallinity. In irradiated PE-UHMW (1020g, 1050g, Dsa, Lsa, X3sa) the toughness level is significantly lower. Molar mass, degree of crystallinity, and the crosslinks in the amorphous phase superpose. The resulting material behavior is complex and does not allow explicit classification of effects. The $X3^{TM}$ material (X3sa) shows higher fracture toughness (than Dsa and Lsa), especially in terms of J_{0.2}. A low content of small lamellae fractions characterizes this material state. Hence, the influence of LTD on the fracture behavior should be further investigated by systematic variations of the content of small lamellae. Generally, fracture toughness in semi-crystalline polymers is influenced by the amorphous phase and the concentration of load transferring tie molecule and entanglements. In the investigated PE-UHMW material states $J_{0.2}$ and $dJ/d\Delta a \mid_{0.2}$ values are not directly influenced by structural parameters at nanometer scale (e.g. thickness of the amorphous phase l_a), the probability of occurrence of tie molecules, and the tie-molecule and entanglement area fraction at the crystalline-amorphous interface. One reason can be that the fracture mechanism in PE-UHMW does not involve cavitations ahead of the crack tip (unlike other PE types). Crack initiation and stable crack growth are influenced by the characteristics of the amorphous phase: as the mobility of the amorphous phase decreases (in terms of increasing temperature at onset of crystallization T_{c,onset}) fracture toughness decreases. Higher concentration of a polymer chain end-group - the terminal vinyl group (TermVI) - results in higher fracture toughness in all material states (even though Y-crosslinking and high temperatures during consolidation influence the TermVI contrary). Especially in GUR1050 a low TermVI accompanies low fracture toughness. The stable crack growth strongly correlates with TermVI and T_{c,onset}. Furthermore, higher total irradiation dose (in terms of TVI) results in higher resistance against stable crack growth. The J_{0.2} values are not directly influenced by TVI. If the "quality" of the amorphous phase is combined with its availability during crack initiation (TermVI multiplied by l_a) increasing values correlate with increasing $J_{0.2}$.

Generally, the aim for optimization of PE-UHMW in load bearing implants is maximum resistant against oxidative degradation, maximum toughness, and minimum *in vivo* wear. The investigations on the first two topics in this Thesis suggest:

- Consolidation: Compression molding and ram extrusion lead to material states with similar bulk morphology and mechanical properties. Compression molding leads to a priori more homogenous material. The outer layers of the ram extruded rod are damaged during consolidation. Although these layers are probably milled away during the further processing, the risk of containing oxidative degradation products (which can act as precursors for further oxidation) is lower in compression molded PE-UHMW. The TermVI gives additional information on the consolidation process and should be used in quality control routinely. The correlation of TermVI and fracture toughness can be used to further optimize the consolidation processes.
- Molar mass and additivation with vitamin E: The higher molar mass in GUR 1050 results in lower degree of crystallinity, lower micro-hardness and indentation modulus compared with lower molar mass GUR 1020. The addition of vitamin E does not change structural parameters and mechanical properties substantially. Molar mass does not affect fracture toughness within the scope of this thesis. From polymer technology aspect, the PE-UHME grades (GUR 1020, GUR 1020VitE, GUR 1050) are similarly qualified for use in hip implants.
- Crosslinking: PE-UHMW for use in total hip arthroplasty has to be crosslinked in order to enhance *in vivo* wear behavior and hence, longevity of the implant. It is no option to use non-crosslinked material at the moment, although the resistance against crack growth is lower in these material states. Based on the investigations in this thesis future crosslinking procedures may be:
 - Stabilization of the material after irradiation by annealing and the use of Vitamin E: The material is protected from further oxidation by Vitamin E. Annealed material shows higher fracture toughness than remelted PE-UHMW.
 - Optimization of LTD: Preservation of the perfection of the lamellae by annealing prior to irradiation (leading to bigger lamellae). After irradiation stabilization of the material by remelting and annealing: During irradiation the crosslinks are formed in the amorphous phase. Remelting stabilizes effectively against oxidative degradation and it releases longer chain segments which can probably form bigger lamellae again during crystallization. The final annealing step reduces the amount of small lamellae in the material. The use of Vitamin E may protect the material additionally during *in vivo* use. The effects of this processing route on structure, mechanical properties, and fracture toughness (and wear) have to be investigated.

Another possibility is to investigate new crosslinking methods which do not involve irradiation crosslinking in order to avoid the susceptibility to oxidative degradation. These routes involve higher research and development costs, as PE-UHMW crosslinked by other methods than irradiation with gamma-rays and electron beam are not approved by regulatory agencies, e.g. the Food and Drug Administration (FDA).

- Milling and cleaning has no effect on the structure and the properties of PE-UHMW.
- Sterilization: Irradiation should not be used for sterilization purpose. Radicals generated in this final step are not stabilized the material is susceptible to oxidation and the fracture toughness is reduced. Gas sterilization methods are preferable as no radicals are generated.
- Shelf live: PE-UHMW which contains free radicals oxidizes as soon as oxygen is available. Liners containing free radicals should be packaged in barrier packaging containing the lowest concentration of oxygen possible for as long as possible.

Thus, the correlations of the structure properties in PE-UHMW are far less understood than it is commonly expected due to the simple constitution of the polymer. Further basic research is worthwhile for optimization of PE-UHMW for total joint replacement.

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A Appendix

A.4.1 Comparison of the material states and correlation of structural parameters with mechanical properties

Table A.4.1-1: Comparison of the investigated material states, FTIR data: OI – oxidation index, TVI – trans vinylene index, TermVI – terminal vinylene index, X_{FTIR} – degree of crystallinity calculated from FTIR data; n.a. – not analyzable, m – mean value, s – standard deviation

sample	OI (-)		TVI (-)		TermVI (-)		X _{FTIR} (%)	
	m	s	m	s	m	s	m	Ś
RER (bulk)	0.005	0.003	n.a.	n.a.	0.008	0.001	55.9	0.4
CMS	0.011	0.003	n.a.	n.a.	0.008	0.001	55.4	0.2
GUR1050	0.006	0.005	n.a.	n.a.	0.005	0.001	56.6	0.2
GUR1020	n.a.	n.a.	n.a.	n.a.	0.009	0.001	60.2	0.4
GUR1020VitE	n.a.	n.a.	n.a.	n.a.	0.010	0.001	59.9	0.1
1020ng	0.005	0.005	n.a.	n.a.	0.009	0.001	60.2	0.7
1050ng	0.002	0.002	n.a.	n.a.	0.009	0.001	56.9	0.1
1020g	0.016	0.008	0.013	0.001	0.004	0.001	61.8	0.3
1050g	0.021	0.011	0.011	0.001	0.004	0.001	58.7	0.3
Dsa	0.005	0.004	0.053	0.002	0.004	0.001	52.5	0.4
Lsa	0.011	0.009	0.038	0.002	0.003	0.001	53.0	0.2
X3sa	0.047	0.008	0.029	0.002	0.002	0.001	64.0	0.3
GAN bulk (D)	0.003	0.003	0.048	0.003	n.a.	n.a.	52.5	0.4
FIN bulk (X3)	0.078	0.007	0.029	0.003	0.003	0.002	63.6	0.3
MAS bulk (irrPE)	0.025	0.006	0.015	0.006	0.004	0.002	63.8	0.6
MAS ox max (irr PE)	2.349	0.158	0.018	0.005	0.002	0.002	74.8	0.3

Table A.4.1-2: Comparison of the investigated material states, DSC data: T_{m1} – melting point in the first heating run, T_{m2} – melting point in the second heating run, T_c – minimum temperature during crystallisation, $T_{c, onset}$ – temperature at the beginning of the crystallisation; m - mean value, s – standard deviation;

sample	T _{m1} (°C)		T _{m2} (°C)		T _c (°C)		T _{c, onset} (°C)	
	m	S	m	S	m	S	m	S
RER (bulk)	133.5	0.2	131.3	0.1	120.2	0.1	122.3	0.1
CMS	134.0	0.2	131.2	0.1	119.9	0.1	122.1	0.1
GUR1050	134.1	0.1	131.1	0.2	120.5	0.2	122.6	0.2
GUR1020	134.5	0.2	131.6	0.1	121.0	0.1	123.2	0.2
GUR1020VitE	134.3	0.1	131.3	0.1	120.8	0.1	122.8	0.1
1020ng	134.8	0.2	131.7	0.2	121.3	0.1	123.4	0.1
1050ng	134.0	0.1	131.2	0.1	120.2	0.1	122.1	0.1
1020g	136.6	0.1	129.5	0.1	120.4	0.1	126.3	0.1
1050g	135.9	0.2	129.4	0.2	119.9	0.1	126.4	0.4
Dsa	137.4	0.2	136.3	0.2	128.4	0.3	131.5	0.3
Lsa	136.2	0.1	134.8	0.1	127.1	0.1	130.9	0.1
X3sa	138.7	0.2	133.4	0.3	125.4	0.3	129.7	0.4
GAN bulk (D)	137.3	0.1	136.4	0.1	128.8	0.3	131.6	0.3
FIN bulk (X3)	138.4	0.4	132.5	1.3	125.0	0.2	129.3	0.2
MAS bulk (irrPE)	136.6		130.9		121.2		127.4	
MAS ox max (irr PE)	136.3	0.1	131.9	0.0	121.4	0.0	123.8	0.4

Table A.4.1-3: Comparison of the investigated material states, DSC data: $X_{DSC, 1}$ – degree of crystallinity calculated from the first DSC heating run, $X_{DSC, 2}$ – degree of crystallinity calculated from the second DSC heating run, l_c – mean lamellar thickness calculated from the first heating run, p – probability pf occurrence of tie molecules calculated from the first heating run (see equation 1), F_s – tie molecule and entanglement area fraction at the crystal-amorphous interface calculated from the first heating run (see equation 13); n.a. – not analyzable, m - mean value, s – standard deviation;

sample	X _{DSC, 1} (%)		X _{DSC, 2} (%)		l _c (nm)			
	m	S	m	S	m	S	р	Fs
RER (bulk)	53.3	0.9	51.6	1.0	22.4	0.4	0.325	0.572
CMS	54.1	0.8	51.1	0.8	23.5	0.4	0.324	0.580
GUR1050	53.2	1.5	49.2	1.1	23.5	0.1	0.324	0.569
GUR1020	54.2	0.9	50.3	1.0	24.6	0.3	0.315	0.566
GUR1020VitE	56.7	0.8	51.4	0.4	24.1	0.3	0.316	0.600
1020ng	61.9	0.7	56.9	0.7	25.2	0.5	0.317	0.683
1050ng	58.0	1.0	54.3	0.9	23.5	0.2	0.325	0.638
1020g	65.0	0.6	55.3	0.6	30.7	0.3	0.307	0.720
1050g	61.3	0.6	54.0	0.9	28.3	0.6	0.321	0.683
Dsa	51.0	1.2	49.2	0.9	33.8	0.9	0.304	0.510
Lsa	47.9	1.0	45.6	0.8	29.3	0.4	0.311	0.491
X3sa	60.3	1.4	48.7	1.1	40.9	1.0	0.270	0.559
GAN bulk (D)	53.2	2.3	51.0	2.4	33.4	0.3	0.307	0.539
FIN bulk (X3)	59.0	1.4	48.1	1.1	39.1	2.7	0.274	0.551
MAS bulk (irrPE)	65.5		54.1		30.7		0.307	0.733
MAS ox max (irr PE)	75.1	0.3	61.6	0.1	29.5	0.2	n.a.	n.a.

Table A.4.1-4: Comparison of the investigated material states, DSI data and data from fracture mechanical tests: hardness H_{IT} (MPa) and indentation modulus E_{IT} (MPa), $J_{0.2}$ – technical crack initiation value = value of the J-Integral at crack extension of 0.2 mm (kJ/m²); n.a. – not analyzable, m – mean value, s – standard deviation

sample	H _{IT} (MPa)		Е _{іт} (MPa)		J _{0.2} (kJ/m ²)		dJ/d∆a _{0.2} (× 1000 kJ/m³)	
	m	S	m	S	m	S	m	S
RER (bulk)	44.1	1.9	748.7	25.2	55.3	4.4	243.3	19.0
CMS	40.2	1.8	748.5	32.7	n.a.	n.a.	n.a.	n.a.
GUR1050	52.0	1.8	984.2	29.4	40.5	4.8	285.1	26.6
GUR1020	55.5	1.8	932.2	31.0	63.6	10.8	325.4	5.4
GUR1020VitE	48.5	3.0	888.8	21.6	72.6	12.0	157.9	9.3
1020ng	54.8	2.9	961.0	35.2	51.8	6.3	245.7	33.9
1050ng	48.3	1.9	886.5	26.9	67.6	8.2	324.4	16.2
1020g	59.9	1.8	1051.3	23.5	18.0	4.0	81.7	6.8
1050g	49.2	1.4	891.1	19.1	24.7	5.5	119.0	16.1
Dsa	40.5	1.7	702.9	15.8	25.5	5.4	66.0	8.5
Lsa	44.8	2.3	734.6	30.2	24.6	5.4	64.9	10.1
X3sa	57.1	1.7	1074.7	29.2	34.8	7.1	85.6	13.0
GAN bulk (D)	42.3	2.0	702.1	33.7	n.a.	n.a.	n.a.	n.a.
FIN bulk (X3)	57.1	3.4	1065.1	40.6	n.a.	n.a.	n.a.	n.a.
MAS bulk (irrPE)	59.4	2.5	1217.9	40.0	n.a.	n.a.	n.a.	n.a.
MAS ox max (irr PE)	93.8	3.8	2436.4	96.4	n.a.	n.a.	n.a.	n.a.



Figure A.4.1-1: Comparison of the investigated PE-UHMW material states, DSC data: p – probability of occurrence of tie molecules calculated from the first heating run



Figure A.4.1-2: Correlation of p – probability of occurrence of tie molecules calculated from the first DSC heating run with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-3: Correlation of p – probability of occurrence of tie molecules to l_p - the long period, both calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-4: Correlation of F_s – tie molecule and entanglement area fraction at the crystalamorphous interface calculated from the first DSC heating run with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-5: Comparison of the investigated PE-UHMW material states, DSI data: H_{IT} (MPa) – micro hardness



Figure A.4.1-6: Comparison of the investigated PE-UHMW material states, DSI data: E_{IT} (MPa) – indentation modulus



Figure A.4.1-7: Correlation of H_{IT} - micro hardness with molar mass of the investigated PE-UHMW material states



Figure A.4.1-8: Correlation of E_{IT} – indentation modulus with molar mass of the investigated PE-UHMW material states



Figure A.4.1-9: Correlation of H_{IT} - micro hardness with l_c – average lamellar thickness calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-10: Correlation of H_{IT} – indentation modulus with TermVI – terminal vinyl index of the investigated PE-UHMW material states



Figure A.4.1-11: Correlation of E_{IT} – indentation modulus with TermVI – terminal vinyl index of the investigated PE-UHMW material states



Figure A.4.1-12: Correlation of H_{IT} – indentation modulus with $T_{c,onset}$ – the temperature at beginning of crystallization of the investigated PE-UHMW material states



Figure A.4.1-13: Correlation of EIT – indentation modulus with Tc,onset – the temperature at beginning of crystallization of the investigated PE-UHMW material states



Figure A.4.1-14: Correlation of H_{IT} - micro hardness with p – probability of occurrence of tie molecules calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-15: Correlation of E_{IT} – indentation modulus with p – probability of occurrence of tie molecules calculated from the first DSC heating run of the investigated PE-UHMW material states



consolidation (RER) molar mass and additivation (GUR 1020, GUR 1020VitE, GUR 1050) manufacturing (1020ng, 1050ng) gamma-sterilization (102g, 1050g)

- crosslinking (Dsa, Lsa, X3sa)
- in vivo (GAN, FIN, MAS)

Figure A.4.1-16: Correlation of H_{IT} - micro hardness with F_s - tie molecule area fraction at the crystalamorphous interface calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-17: Correlation of E_{IT} – indentation modulus with F_s – tie molecule area fraction at the crystal-amorphous interface calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-18: Ram extruded rod RER – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-19: GUR 1050 – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-20: GUR 1020 – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-21: GUR 1020VitE – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-22: virgin implants, GUR 1020, non gamma-sterilized (1020ng) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-23: virgin implants, GUR 1050, non gamma-sterilized (1050ng) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-24: virgin implants, GUR 1020, gamma-sterilized (1020g) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-25: virgin implants, GUR 1050, gamma-sterilized (1050g) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-26: virgin implants, Durasul® (Dsa) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-27: virgin implants, LongevityTM (Lsa) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-28: virgin implants, X3 (X3sa) – J-R-curves of all experiments (arc-shaped specimens)



Figure A.4.1-29: Comparison of the $J_{0,2}$ – technical crack initiation (arc shaped specimens) and a_{12n} - impact toughness (data provided by Orthoplastics, specimens notched at two sides)



Figure A.4.1-30: Correlation of $J_{0,2}$ – technical crack initiation with molar mass of the investigated PE-UHMW material states



Figure A.4.1-31: Correlation of stable crack growth parameter $dJ/d\Delta a|_{0.2}$ with molar mass of the investigated PE-UHMW material states



Figure A.4.1-32: Correlation of $J_{0,2}$ – technical crack initiation with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-33: Correlation of stable crack growth parameter $dJ/d\Delta a|_{0.2}$ with the degree of crystallinity calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-34: Correlation of $J_{0.2}$ – technical crack initiation with l_c – average lamellar thickness calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-35: Correlation of stable crack growth parameter $dJ/d\Delta a|_{0.2}$ with l_c – average lamellar thickness calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-36: Correlation of $J_{0,2}$ – technical crack initiation with l_p – long period calculated from the first DSC heating run of the investigated PE-UHMW material states



Figure A.4.1-37: Correlation of stable crack growth parameter $dJ/d\Delta a|_{0,2}$ with l_p – long period calculated from the first DSC heating run of the investigated PE-UHMW material states

A.4.2 Anisotropy induced during life cycle of PE-UHMW hip components

A.4.2.1 Results from FTIR measurements

A.4.2.1.1 Depth profiles of TVI, TermVI, and OI



Figure A.4.2.1-1: FTIR data: comparison of terminal vinylene index (TermVI) from compression molded sheet (CSM) and ram extruded rod (RER) from surface areas inwards (in the case of RER, from area A and B)



Figure A.4.2.1-2: FTIR data: comparison of oxidation index (OI) and terminal vinylene index (TermVI) of GUR 1020, GUR 1020 VitE and GUR 1050 from surface areas inwards



Figure A.4.2.1-3: FTIR data: comparison of oxidation index (OI) and terminal vinylene index (TermVI) of virgin implant, GUR 1020, non gamma-sterilized (1020ng), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-4: FTIR data: comparison of oxidation index (OI) and terminal vinylene index (TermVI) of virgin implant, GUR 1050, non gamma-sterilized (1050ng), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-5: FTIR data: comparison of oxidation index (OI), terminal vinylene index (TermVI), and trans vinylene index (TVI) of virgin implant, GUR 1020, gamma-sterilized (1020g), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-6: FTIR data: comparison of oxidation index (OI), terminal vinylene index (TermVI), and trans vinylene index (TVI) for virgin implant, GUR 1050, gamma-sterilized (1050g), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-7: FTIR data: comparison of oxidation index (OI), terminal vinylene index (TermVI), and trans vinylene index (TVI) for Durasul® (Dsa), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-8: FTIR data: comparison of oxidation index (OI), terminal vinylene index (TermVI), and trans vinylene index (TVI) for LongevityTM (Lsa), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-9: FTIR data: comparison of oxidation index (OI), terminal vinylene index (TermVI), and trans vinylene index (TVI) for X3 (X3sa), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-10: FTIR data: comparison of trans vinylene index (TVI) for in vivo used explant made from Durasul® (GAN), center unloaded, center loaded, and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-11: FTIR data: comparison of trans vinylene index (TVI) and terminal vinylene index (TermVI) for in vivo used explant made from X3 (FIN), center loaded, and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-12: FTIR data: comparison of trans vinylene index (TVI) and terminal vinylene index (TermVI) for in vivo used explant made from irradiation sterilized PE-UHMW (MAS), rim area from inner (IO) and outer (AO) surface inwards

A.4.2.1.2 Depth profiles of degree of crystallinity



Figure A.4.2.1-13: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra of GUR 1020, GUR 1020 VitE and GUR 1050 from surface areas inwards



Figure A.4.2.1-14: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for virgin implant, GUR 1020, non gamma-sterilized (1020ng), center and rim areas from inner (IO) and outer (AO) surface inwards


Figure A.4.2.1-15: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for virgin implant, GUR 1050, non gamma-sterilized (1050ng), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-16: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for virgin implant, GUR 1020, gamma-sterilized (1020g), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-17: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for virgin implant, GUR 1050, gamma-sterilized (1050g), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-18: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for Durasul® (Dsa), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-19: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for LongevityTM (Lsa), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-20: FTIR data: comparison of the degree of crystallinity calculated from the FTIR spectra for X3 (X3sa), center and rim areas from inner (IO) and outer (AO) surface inwards

A.4.2.1.3 Differences between rim and center areas, inner and outer surface



Figure A.4.2.1-21: FTIR data: comparison of the mean values of oxidation index (OI), terminal vinylene index (TermVI), and degree of crystallinity (X_{FTIR}) for virgin implants, GUR 1020 and GUR 1050, non gamma-sterilized (1020ng, 1050ng), center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-22: FTIR data: comparison of the mean values of oxidation index (OI), terminal vinylene index (TermVI), trans vinylene index (TVI) and degree of crystallinity for 1020g and 1050g, center and rim areas from inner (IO) and outer (AO) surface inwards



Figure A.4.2.1-23: FTIR data: comparison of the mean values of oxidation index (OI), terminal vinylene index (TermVI), trans vinylene index (TVI) and degree of crystallinity for Durasul® (Dsa), LongevityTM (Lsa), and X3TM (X3sa), center (c) and rim (r) areas from inner (IO) and outer (AO) surface inwards





Figure A.4.2.1-24: Ram extruded rod RER - FTIR mapping form surface area B inwards: carbonyl region



Figure A.4.2.1-25: Compression molded sheet CMS - FTIR mapping: carbonyl region



Figure A.4.2.1-26: GUR 1020 containing 0.1%wt Vitamin E - FTIR mapping: carbonyl region



Figure A.4.2.1-27: Virgin implant, GUR 1020, non gamma-sterilized (1020ng1) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-28: Virgin implant, GUR 1020, non gamma-sterilized (1020ng) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-29: Virgin implant, GUR 1020, non gamma-sterilized (1020ng) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-30: Virgin implant, GUR 1050, non gamma-sterilized (1050ng) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-31: Virgin implant, GUR 1050, non gamma-sterilized (1050ng) - FTIR mapping center inner surface: carbonyl region



Figure A.4.2.1-32: Virgin implant, GUR 1050, non gamma-sterilized (1050ng) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-33: Virgin implant, GUR 1050, non gamma-sterilized (1050ng) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-34: Virgin implant, GUR 1020, gamma-sterilized (1020g) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-35: Virgin implant, GUR 1020, gamma-sterilized (1020g) - FTIR mapping center inner surface: carbonyl region



Figure A.4.2.1-36: Virgin implant, GUR 1020, gamma-sterilized (1020g) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-37: Virgin implant, GUR 1020, gamma-sterilized (1020g) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-38: Virgin implant, GUR 1050, gamma-sterilized (1050g) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-39: Virgin implant, GUR 1050, gamma-sterilized (1050g) - FTIR mapping center inner surface: carbonyl region



Figure A.4.2.1-40: Virgin implant, GUR 1050, gamma-sterilized (1050g) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-41: Virgin implant, Durasul® (Dsa) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-42: Virgin implant, Durasul® (Dsa) - FTIR mapping center inner surface: carbonyl region



Figure A.4.2.1-43: Virgin implant, Durasul® (Dsa) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-44: Virgin implant, Durasul® (Dsa) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-45: Virgin implant, LongevityTM (Lsa) - FTIR mapping center inner surface: carbonyl region



Figure A.4.2.1-46: Virgin implant, LongevityTM (Lsa) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-47: Virgin implant, LongevityTM (Lsa) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-48: Virgin implant, X3 (X3sa) - FTIR mapping center outer surface: carbonyl region



Figure A.4.2.1-49: Virgin implant, X3 (X3sa) - FTIR mapping rim outer surface: carbonyl region



Figure A.4.2.1-50: Virgin implant, X3 (X3sa) - FTIR mapping rim inner surface: carbonyl region



Figure A.4.2.1-51: *In vivo* used explant made from X3TM (FIN) - FTIR mapping rim outer surface: carbonyl region

A.4.2.1 Results from DSC measurements

A.4.2.1.1 Depth profiles of characteristic temperatures



Figure A.4.2.1-1: Compression molded sheet CMS - DSC data: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallization temperature (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$



Figure A.4.2.1-2: Ram extruded rod RER – DSC data from surface area A inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-3: GUR 1050 - DSC data: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-4: GUR 1020 - DSC data: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-5: GUR 1020VitE - DSC data: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-6: virgin implant, GUR 1020, non gamma-sterilized (1020ng), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-7: virgin implant, GUR 1020, non gamma-sterilized (1020ng), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-8: virgin implant, GUR 1050, non gamma-sterilized (1050ng), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}), the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation ($T_{c, onset}$)



Figure A.4.2.1-9: virgin implant, GUR 1050, non gamma-sterilized (1050ng), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-10: virgin implant, GUR 1020, gamma-sterilized (1020g), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-11: virgin implant, GUR 1020, gamma-sterilized (1020g), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-12: virgin implant, GUR 1050, gamma-sterilized (1050g), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-13: virgin implant, GUR 1050, gamma-sterilized (1050g), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-14: virgin implant, Durasul® (Dsa), center – DSC data from outer surface (AO) and inner surface (IO)area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-15: virgin implant, Durasul[®] (Dsa), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-16: virgin implant, LongevityTM (Lsa), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}), the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation ($T_{c, onset}$)



Figure A.4.2.1-17: virgin implant, LongevityTM (Lsa), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{ml}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-18: virgin implant, X3 (X3sa), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-19: virgin implant, X3 (X3sa), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-20: In vivo used explant made from Durasul® (GAN), center loaded – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-21: In vivo used explant made from Durasul® (GAN), center unloaded – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}), the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation ($T_{c, onset}$)



Figure A.4.2.1-22: In vivo used explant made from Durasul® (GAN), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-23: In vivo used explant made from X3 (FIN), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallisation temperature (T_c) and the temperature at the beginning of the crystallisation $(T_{c, onset})$



Figure A.4.2.1-24: In vivo used explant made from irradiation sterilized PE-UHMW (MAS), rim – DSC data from inner surface area inwards: comparison of the melting point in the first (T_{m1}) and second heating run (T_{m2}), the crystallization temperature (T_c) and the temperature at the beginning of the crystallization ($T_{c, onset}$)

A.4.2.1.2 Depth profiles of degree of crystallinity calculated from the first and second heating run



Figure A.4.2.1-25: Compression molded sheet CMS and ram extruded rod RER - DSC data: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run



Figure A.4.2.1-26: GUR 1050 - DSC data: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-27: GUR 1020 - DSC data: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run



Figure A.4.2.1-28: GUR 1020VitE - DSC data: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run



Figure A.4.2.1-29: virgin implant, GUR 1020, non gamma-sterilized (1020ng), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-30: virgin implant, GUR 1020, non gamma-sterilized (1020ng), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-31: virgin implant, GUR 1050, non gamma-sterilized (1050ng), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-32: virgin implant, GUR 1050, non gamma-sterilized (1050ng), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-33: virgin implant, GUR 1020, gamma-sterilized (1020g), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-34: virgin implant, GUR gamma-sterilized (1020g), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run



Figure A.4.2.1-35: virgin implant, GUR 1050, gamma-sterilized (1050g), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-36: virgin implant, GUR 1050, gamma-sterilized (1050g), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-37: virgin implant, Durasul[®] (Dsa), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run



Figure A.4.2.1-38: virgin implant, Durasul® (Dsa), rim – DSC data from outer surface (AO) and inner surface (IO)area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run


Figure A.4.2.1-39: virgin implant, LomgevityTM (Lsa), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-40: virgin implant, LomgevityTM (Lsa), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-41: virgin implant, X3 (X3sa), center – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-42: virgin implant, X3 (X3sa), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-43: In vivo used explant made from Durasul® (GAN), center loaded – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-44: In vivo used explant made from Durasul® (GAN), center unloaded – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-45: In vivo used explant made from Durasul® (GAN), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run



Figure A.4.2.1-46: In vivo used explant made from X3 (FIN), rim – DSC data from outer surface (AO) and inner surface (IO) area inwards: comparison of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run

A.4.2.1.3 Differences between rim and center areas, inner and outer surface



Figure A.4.2.1-47: DSC data: comparison of the mean values of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallization temperature (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$, GUR 1020 and GUR 1050, non gamma-sterilized (1020ng1, 1050ng1), center and rim areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-48: DSC data: comparison of the mean values of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run, GUR 1020 and GUR 1050, non gamma-sterilized (1020ng1, 1050ng1), center and rim areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-49: virgin implant, GUR 1020, non gamma-sterilized (1020ng1): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-50: virgin implant, GUR 1050, non gamma-sterilized (1050ng1): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-51: DSC data: comparison of the mean values of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallization temperature (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$, GUR 1020 and GUR 1050, gamma-sterilized (1020g2, 1050g1), center and rim areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-52: DSC data: comparison of the mean values of the degree of crystallinity calculated from the first $(X_{DSC, 1})$ and second $(X_{DSC, 2})$ DSC heating run, GUR 1020 and GUR 1050, gamma-sterilized (1020g2, 1050g1), center and rim areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-53: virgin implant, GUR 1020, gamma-sterilized (1020) a: comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-54: virgin implant, GUR 1050, gamma-sterilized (1050g1): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-55: DSC data: comparison of the mean values of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallization temperature (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$, Durasul® (Dsa3), LongevityTM (Lsa2), and X3 (X3sa1), center (c) and rim (r) areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-56: DSC data: comparison of the mean values of the degree of crystallinity calculated from the first ($X_{DSC, 1}$) and second ($X_{DSC, 2}$) DSC heating run, Durasul® (Dsa3), LongevityTM (Lsa2), and X3 (X3sa1), center (c) and rim (r) areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-57: virgin implant, Durasul® (Dsa3): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-58: virgin implant, LongevityTM (Lsa2): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-59: virgin implant, X3 (X3sa1): comparison of lamellar thickness distribution LTD calculated from the first and the second heating run



Figure A.4.2.1-60: DSC data: comparison of the mean values of the melting point in the first (T_{m1}) and second heating run (T_{m2}) , the crystallization temperature (T_c) and the temperature at the beginning of the crystallization $(T_{c, onset})$, in vivo used explants made from Durasul® (GAN), X3 (FIN), and irradiation sterilized PE-UHMW (MAS), center loaded (cl), center unloaded (cul) and rim (r) areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-61: DSC data: comparison of the mean values of the degree of crystallinity calculated from the first (X_{DSC, 1}) and second (X_{DSC, 2}) DSC heating run, in vivo used explants made from Durasul® (GAN), X3 (FIN), and irradiation sterilized PE-UHMW (MAS), center loaded (cl), center unloaded (cul) and rim (r) areas from inner (IO) and outer (AO) surface



Figure A.4.2.1-62: In vivo used explant made from Durasul®: comparison of lamellar thickness distribution LTD calculated from the first and the second heating run

A.4.2.1.4 LTD



Figure A.4.2.1-63: Compression molded sheet CMS - Lamellar thickness distribution calculated from the first (left) and second (right) heating run



Figure A.4.2.1-64: GUR 1050 - Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-65: GUR 1020 - Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-66: GUR 1020VitE - Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-67: virgin implant, GUR 1020, non gamma-sterilized (1020ng), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-68: virgin implant, GUR 1020, non gamma-sterilized (1020ng), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-69: virgin implant, GUR 1020, non gamma-sterilized (1020ng), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-70: virgin implant, GUR 1020, non gamma-sterilized (1020ng), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-71: virgin implant, GUR 1050, non gamma-sterilized (1050ng), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-72: virgin implant, GUR 1050, non gamma-sterilized (1050ng), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-73: virgin implant, GUR 1050, non gamma-sterilized (1050ng), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-74: virgin implant, GUR 1050, non gamma-sterilized (1050ng), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first heating run (left) and the second heating run (right)



Figure A.4.2.1-75: virgin implant, GUR 1020, gamma-sterilized (1020g), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-76: virgin implant, GUR 1020, gamma-sterilized (1020g), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-77: virgin implant, GUR 1020, gamma-sterilized (1020g), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-78: virgin implant, GUR 1020, gamma-sterilized (1020g), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-79: virgin implant, GUR 1050, gamma-sterilized (1050g), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-80: virgin implant, GUR 1050, gamma-sterilized (1050g), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-81: virgin implant, GUR 1050, gamma-sterilized (1050g), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-82: virgin implant, GUR 1050, gamma-sterilized (1050g), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-83: virgin implant, Durasul® (Dsa), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-84: virgin implant, Durasul® (Dsa), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-85: virgin implant, Durasul® (Dsa), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-86: virgin implant, Durasul® (Dsa), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-87: virgin implant, LongevityTM (Lsa), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-88: virgin implant, LongevityTM (Lsa), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-89: virgin implant, LongevityTM (Lsa), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-90: virgin implant, X3 (X3sa), center – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-91: virgin implant, X3 (X3sa), center – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-92: virgin implant, X3 (X3sa), rim – DSC data from outer surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-93: In vivo used explant made from Durasul® (GAN), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-94: In vivo used explant made from Durasul® (GAN), center loaded – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run



Figure A.4.2.1-95: In vivo used explant made from X3 (FIN), rim – DSC data from inner surface area inwards: Lamellar thickness distribution LTD calculated from the first (left) and second (right) heating run

A.4.2.3 Results from DSI measurements





Figure A.4.2.3-1: GUR 1020, GUR 1020VitE and GUR 1050; comparison of microhardness H_{IT} (left) and indentation modulus E_{IT} (right) as a function from the distance from surface

Table A.4.2.3-1: Virgin implants, GUR 1020 and GUR 1050 (1020ng and 1050ng): overview about areas and surfaces from which depth profiles of H_{IT} and E_{IT} were recorded; X – location where a depth profile was recorded, IO – from inner surface inwards, AO – from outer surface inwards;

area and surface	1020ng	1050ng
center, AO	Х	
center, IO	Х	Х
rim, AO		
rim, IO	Х	Х



Figure A.4.2.3-2: virgin implant, GUR 1050, non gamma-sterilized (1050ng) – comparison of microhardness H_{IT} (left) and of indentation modulus E_{IT} (right) as a function from the distance from surface; IO ... inner surface



Figure A.4.2.3-3: virgin implant, GUR 1020, non gamma-sterilized (1020ng) – comparison of microhardness H_{IT} (left) and of indentation modulus E_{IT} (right) as a function from the distance from surface; AO ... outer surface, IO ... inner surface

Table A.4.2.3-2: Virgin implants, GUR 1020 and GUR 1050, gamma-sterilized (1020g and 1050g): overview about areas and surfaces from which depth profiles of H_{IT} and E_{IT} were recorded; X – location where a depth profile was recorded, IO – from inner surface inwards, AO – from outer surface inwards,

area and surface	1020g	1050g
center, AO	Х	
center, IO		
rim, AO		
rim, IO	Х	Х



Figure A.4.2.3-4: virgin implant, GUR 1020 and GUR1050, gamma-sterilized (1020g and 1050g) – comparison of microhardness H_{IT} (left) and indentation modulus E_{IT} (right) as a function from the distance from surface; AO ... outer surface, IO ... inner surface

Table A.4.2.3-3: Virgin implants made from crosslinked PE-UHMW (Dsa, Lsa and Xsa): overview about areas and surfaces from which depth profiles of H_{IT} and E_{IT} were recorded; X – location where a depth profile was recorded, IO – from inner surface inwards, AO – from outer surface inwards,

area and surface	Dsa	Lsa	X3sa
center, AO	Х	Х	Х
center, IO			
rim, AO			
rim, IO	Х	Х	



Figure A.4.2.3-5: virgin implants, Durasul[®], LongevityTM, and X3 (Dsa, Lsa, and X3sa) – comparison of microhardness (MPa) as a function from the distance from surface; c ... center, r ... rim, AO ... outer surface, IO ... inner surface



Figure A.4.2.3-6: virgin implants, Durasul®, LongevityTM, and X3 (Dsa3, Lsa2, and X3sa1) – comparison of indentation modulus (MPa) as a function from the distance from surface; c ... center, r ... rim, AO ... outer surface, IO ... inner surface

Table A.4.2.3-4: in vivo used explants made from crosslinked PE-UHMW (GAN and FIN) and irradiation sterilized PE-UHMW (MAS): overview about areas and surfaces from which depth profiles of H_{IT} and E_{IT} were recorded; X – location where a depth profile was recorded, IO – from inner surface inwards, AO – from outer surface inwards,

area and surface	GAN	FIN	MAS
center loaded, AO	Х		
center loaded, IO	Х		
center unloaded, AO			
center unloaded, IO	Х		
rim, AO		Х	
rim, IO	XX	X	XX



Figure A.4.2.3-7: In vivo used explant made from Durasul® (GAN) – comparison of microhardness (MPa) as a function from the distance from surface; AO ... outer surface, IO ... inner surface



Figure A.4.2.3-8: In vivo used explant made from Durasul® (GAN) – comparison of indentation modulus (MPa) as a function from the distance from surface; AO ... outer surface, IO ... inner surface

A.4.2.3.2 Differences between rim and center areas, inner and outer surface



Figure A.4.2.3-9: DSI data: comparison of the mean values of the degree of H_{IT} and E_{IT} , GUR 1020 and GUR 1050, non gamma-sterilized (1020ng1, 1050ng1), center and rim areas from inner (IO) and outer (AO) surface



Figure A.4.2.3-10: DSI data: comparison of the mean values of microhardness and indentation modulus, Durasul®, LongevityTM, and X3 (Dsa3, Lsa2, and X3sa1), center (c) and rim (r) areas from inner (IO) and outer (AO) surface; c ... center, r ... rim

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