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Comparison of conventional and crosslinked ultra high molecular weight polyethylene (UHMWPE) used in hip implant

Anna Laska

Institute of Materials Science and Technology, Lodz University of Technology,
1/15 Stefanowskiego Str., 90-924 Lodz, Poland

E-mail address: annalaska@dokt.p.lodz.pl

ABSTRACT

Since the 1960s UHMWPE has been the material of choice for bearing surfaces in total hip replacements. In spite of its clinical success over years, a large number of necessary revisions has been recently reported. The clinical life span of the hip prostheses is limited by weardebris-induced osteolysis and aseptic loosening. The problem is very complex because of the variety of factors affecting UHMWPE. Nowadays, scientists are working on how optimally adjust the material properties and the implant design in order to increase wear resistance and retain other mechanical properties. The aim of the study is to investigate structural parameters of two UHMWPE material states – conventional (non-crosslinked) and crosslinked. Those types of UHMWPE show slightly different properties, which can affect further behaviour in human body. The comparison between conventional and crosslinked UHMWPE is presented. Differential Scanning Calorimetry (DSC) is the analysis method applied in the research. The structural parameters of UHMWPE are correlated with its mechanical and tribological properties.

Keywords: conventional UHMWPE, crosslinked UHMWPE, acetabular cup, structural parameters, Differential Scanning Calorimetry

1. INTRODUCTION

1. 1. Ultra High Molecular Weight Polyethylene – general overview

Ultra High Molecular Weight Polyethylene (UHMWPE) is a polymer with a very simple chemical composition – only hydrogen and carbon (Figure 1), but its hierarchy of organizational structure at molecular level makes it much more complex [Kurtz 2004]. UHMWPE is formed from ethylene and its molecular chain can contain up to 200,000 ethylene repeat units. Table 1 presents the physical and mechanical properties of UHMWPE with comparison to HDPE. UHMWPE has a very long molecular chain with two types of regions – crystalline (also called crystalline lamellae) and amorphous. Crystalline lamellae are molecules that form ordered and sheetlike regions. Amorphous parts of UHMWPE are disordered. UHMWPE has significant physical and mechanical properties, such as:

- lubricity,
- chemical inertness,
- impact resistance,
- abrasion resistance.

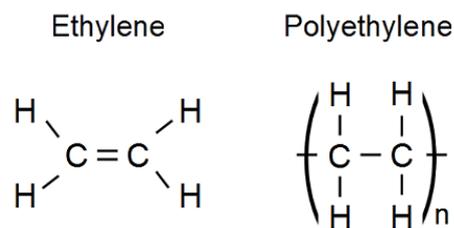


Figure 1. Chemical structure of ethylene and polyethylene.

Table 1. Average physical properties of UHMWPE and HDPE.

Physical property	UHMWPE	HDPE
Molecular weight	2,0 – 6,0	0,05 – 0,25
Melting temperature (°C)	125-138	130-134
Tensile modulus of elasticity (MPa)	800-1600	400-4000
Tensile ultimate strength (MPa)	39-48	22-31
Degree of crystallinity (%)	39-75	60-80

Source: [Kurtz 2004]

UHMWPE has had many medical applications. It has a successful clinical history as a biomaterial and is commonly used for:

- hip replacements,
- knee replacements,
- shoulder replacements,
- spine.

UHMWPE components in orthopedic devices must meet the recommended properties. The characteristics of the UHMWPE should be measured and verified at each processing step – when it is in the form of powder, after consolidation and then exposure of irradiation. Several analytical techniques are developed to assess the desirable properties [Spiegelberg 2016]. The assessed properties may be divided into such main groups as mechanical, chemical, physical and in-vitro properties. Table 2 summarizes chosen test techniques for ready UHMWPE implant.

Table 2. Chosen test techniques for ready UHMWPE implant (after radiation)

Properties	Test Techniques
mechanical	<ul style="list-style-type: none"> • Compression • Fatigue • Small punch
chemical	<ul style="list-style-type: none"> • Fourier Transform Infrared Spectroscopy (FTIR) • Antioxidant concentration
physical	<ul style="list-style-type: none"> • Differential Scanning Calorimetry (DSC) • Scanning electron microscopy (SEM)
in vitro	<ul style="list-style-type: none"> • Accelerated aging • Wear testing

1. 2. Manufacturing and sterilisation

Manufacturing and sterilization processes have great impact on final UHMWPE implants. Therefore, it is essential to adjust production conditions, sterilization type and packaging to obtain the best quality product with the desired physical and mechanical properties.

First of all, UHMWPE is polymerized from ethylene gas [Kelly 2002]. A result of the polymerization is UHMWPE powder. The next step is conversion powder into consolidated forms such as sheets or rods. Semi-finished UHMWPE is produced by compression molding or ram extrusion. That process is performed under elevated temperatures and pressures. Finally, consolidated UHMWPE is machined into its final desirable shape. Before UHMWPE lands in an operating theatre, components must be packaged and sterilized [Jacobs 2007].

Currently, the most popular sterilization methods are:

- ethylene oxide gas sterilization,
- low-temperature gas plasma sterilization,
- gamma inert sterilization and barrier packaging (Gamma radiation dose – 25-40 kGy).

1. 3. Crosslinking

Crosslinking is a method used to enforce UHMWPE implants leading to an decrease in wear rate and less oxidation of the material [Kurtz 2004]. On the other hand, crosslinked materials show lower fracture resistance. Crosslinking is the linking of two (or more) different molecular chains by means of covalent bonds. A result of crosslinking in one long, branched molecule with infinite molecular mass. In the crosslinking of UHMWPE implants, the material is crosslinked with ionizing radiation. For crosslinking processes electron beams (e-beams) and gamma rays are employed. The degree of crosslinking increases with the dose of absorbed irradiation.

1. 4. Hip implant

A prosthesis for total hip replacement (Figure 2) consists of three basic element: stem, head and acetabular cup. Acetabular cup can be either one piece of material or an element consisted of a shell and a liner (Figure 3). Various materials are used in total hip replacement. There are available the following combinations of materials (Table 3) that can be applied in the rotating head and the acetabular cup:

- metal-on-metal,
- ceramic-on-ceramic,
- metal-on-polyethylene,
- ceramic-on-polyethylene.

Table 3. Exemplary materials used in total hip replacement.

metallic materials	<ul style="list-style-type: none"> • Stainless steel • Cobalt-chrome-based alloys (Co-Cr-Mo, Co-Ni-Cr-Mo) • Titanium based alloys (Ti-6Al-4V)
ceramic materials	<ul style="list-style-type: none"> • Silicon nitride • Alumina oxide (Al₂O₃) • Zirconia- toughened alumina (ZTA)
polymeric materials	<ul style="list-style-type: none"> • UHMWPE (conventional or crosslinked) • Carbon fiber (CF)/PEEK • Carbon fiber (CF)/UHMWPE

Source: based on [Ghalme 2016]

Since 1962 UHMWPE is used in total hip replacements. It is well-known that manufacturing, sterilization using irradiation and thermal treatment significantly alter the structure of polymeric material resulting in changes of the mechanical properties of UHMWPE. Crosslinking of UHMWPE has been viewed as a solution to the device failure problem, due to improved wear characteristics. Wear of UHMWPE acetabular cup is a common cause of osteolysis and aseptic loosening of the components. Thus, substantial improvement to the wear resistance of UHMWPE could extend the clinical life span of total hip replacements.

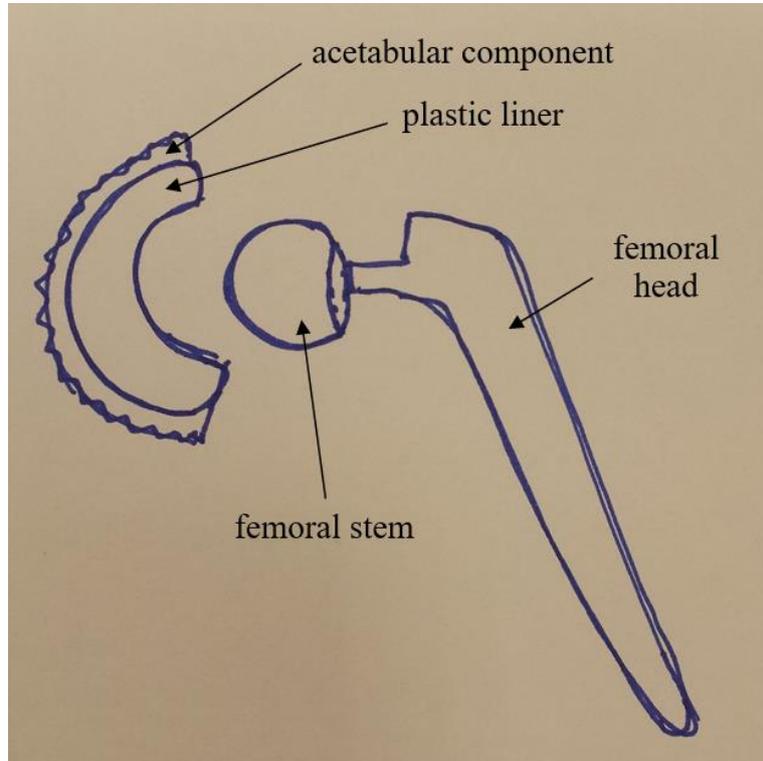


Figure 2. Elements of total hip replacement (source: own picture).



Figure 3. Acetabular cup (plastic liner and metal shell) with femoral stem, removed from a patient body (source: own picture).

2. EXPERIMENTAL

The work concerns an investigations of UHMWPE acetabular cups applied in total hip replacement:

- GUR1050 – the first generation of UHMWPE, conventional one
- Dsa4 – the second generation of UHMWPE, crosslinked one

Both material states were manufactured by use of different method, different thermal treatment was applied. No detailed information was provided by the manufacturers.

In the experiment Differential Scanning Calorimetry (DSC) method was applied to compare two material states. Samples with mass 1-2 mg were prepared. Each piece of the sample was put into an aluminum pan and covered by an aluminum lid. The exact mass of the sample, the pan and the lid was determined using an accurate micro-balance ($\pm 0,01$ mg). Encapsulated UHMWPE samples were ready to be investigated by DSC instrument.

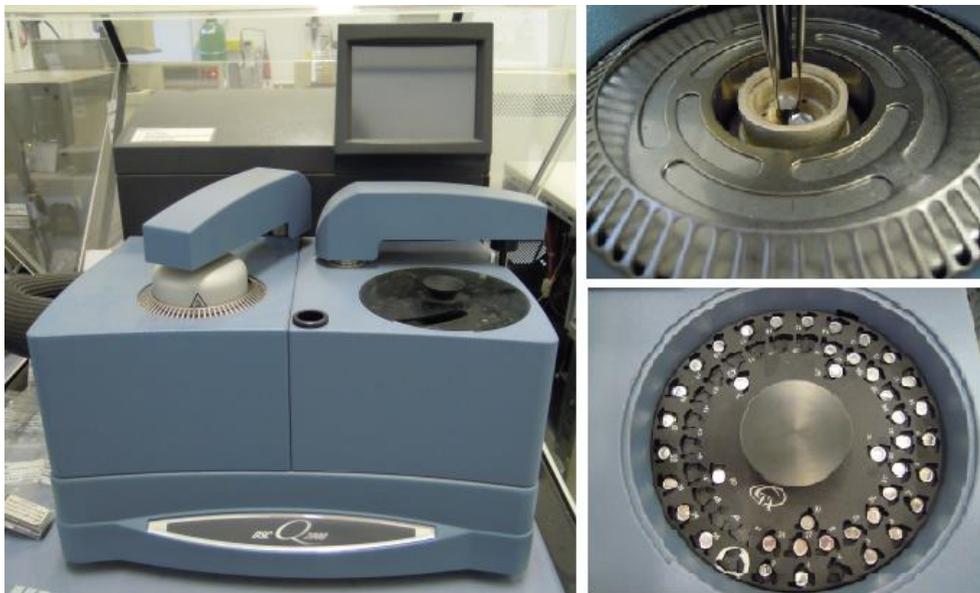


Figure 4. DSC instrument with autoloader.
(source: own picture)

To carry out the measurement a DSC device (TA Instruments, Q2000) was used (Figure 4). The prepared samples were placed into the DSC chamber. The instrument was equipped with an autoloader, which facilitated testing. Every sample was compared with a reference that was an empty aluminum pan with a lid. During the entire experimental part one DSC method was used. Basing [F2625-07] the following temperature program was carried out for all measurements. The procedure started at 0 °C. First of all, the temperature was increased by 10 °C per minute till the temperature was equal to 220 °C. Secondly, that temperature was maintained for 5 minutes. After that isothermal conditions, the temperature decreased with ramps 10 °C per minute until it achieved 0 °C. The next step was a second isothermal state that lasted 5 minutes as well. Finally, the procedure ends with steady temperature growth of

10 °C per minute till 200 °C. Using the software TA Analysis 2000 the information from DSC measurements was analyzed. The following data was obtained (Figure 5):

- melting temperature in first heating run (T_{m1}),
- melting temperature in second heating run (T_{m2}),
- crystallization temperature (T_c),
- onset temperature (T_{onset}).

The results of the experiments were in the form of diagrams. In order to obtain the melting temperatures (first and second heating run) the integration limits were set to 60 °C and 180 °C. In case of crystallization temperature the limits were 40 °C and 180 °C. The onset temperature, which indicates when the crystallization starts, was found to be between the crystallization temperature and the melting temperature after the integration.

Having obtained the data, it was possible to calculate the degree of crystallinity. The heat of fusion of pure UHMWPE (100% crystalline UHMWPE) is a theoretical value. Basing [Kurtz 2004] it is assumed to be equal:

$$\Delta H_f = 291 \frac{J}{g} \quad (1)$$

Degree of crystallinity (X) is calculated according to the formula:

$$X = \frac{\Delta H_{endotherm}}{\Delta H_f} \cdot 100\% \quad (2)$$

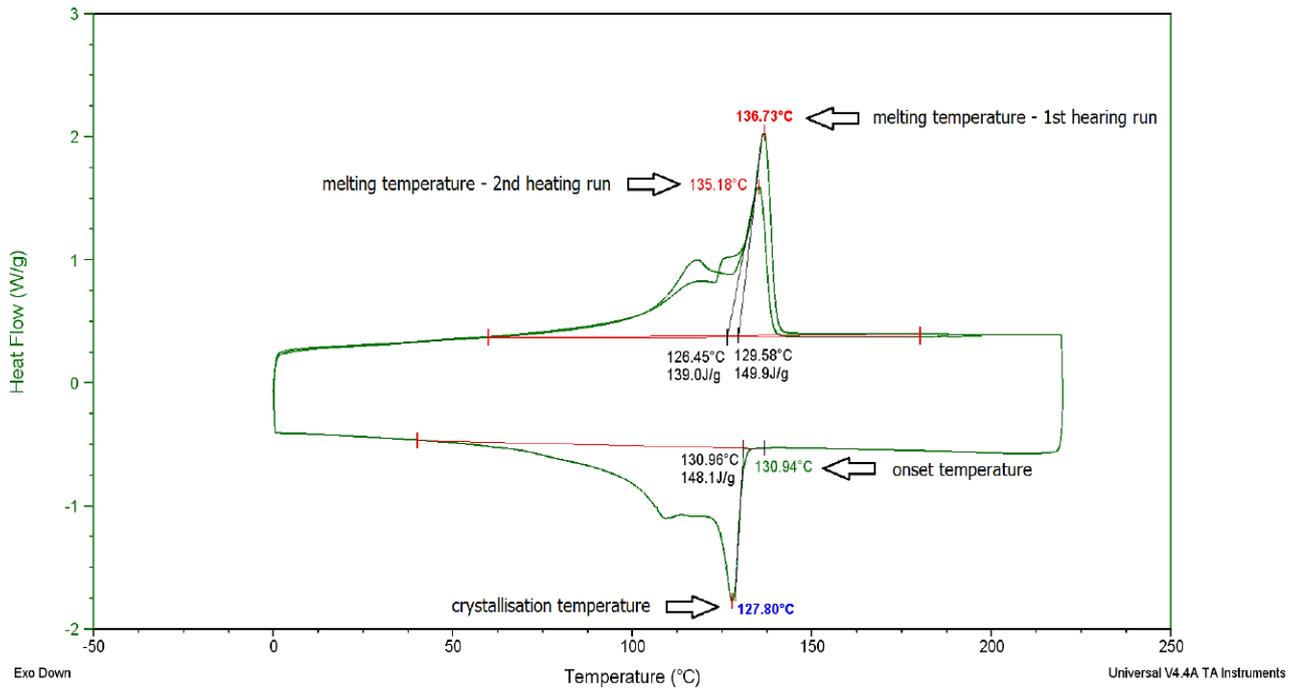


Figure 5. Characteristic temperatures in DSC diagram (source: own picture).

3. RESULTS

The DSC diagrams of two material states (Figure 6) were distinguishable. The materials showed different thermal behavior. The comparison of the mean values of some parameters is presented below in Table 4.

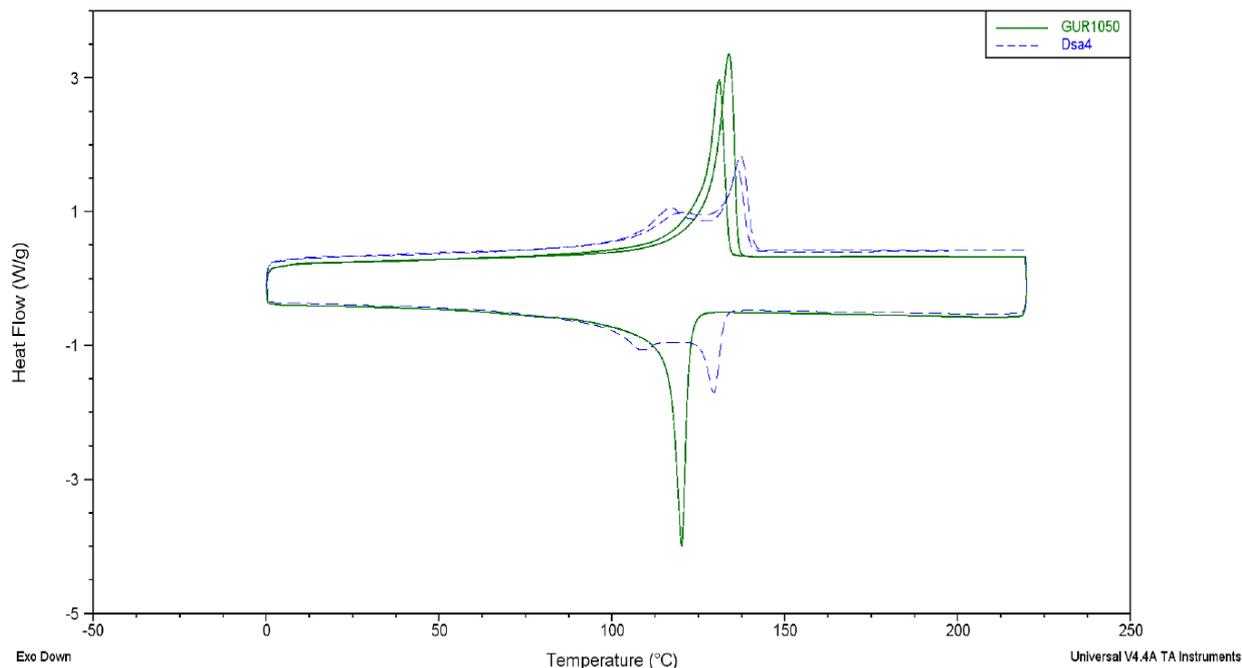


Figure 5. DSC diagrams for both material states (conventional *GUR1050* and crosslinked *Dsa4*).

Dsa 4 (crosslinked UHMWPE) was distinctive by its higher melting temperatures in both heating runs, higher crystallization and onset temperature. However, in comparison to *GUR1050* (conventional one) it had a lower value of degree of crystallization determined by the DSC measurement. In both cases, such parameters as T_m and X_{DSC} were higher in the first heating run than in the second one.

Table 4. Summary of DSC results for both material states.

	conventional UHMWPE <i>GUR1050</i>	crosslinked UHMWPE <i>Dsa4</i>
melting temperature in 1 st heating run [°C]	133,8 ± 0,1	137,2 ± 0,1
melting temperature in 2 nd heating run [°C]	131,0 ± 0,1	136,3 ± 0,1
X_{DSC} in 1 st heating run [%]	55,0 ± 0,6	49,2 ± 0,8

X_{DSC} in 2 nd heating run [%]	$50,8 \pm 0,5$	$47,6 \pm 0,4$
crystallization temperature [°C]	$120,2 \pm 0,1$	$129,3 \pm 0,1$
onset temperature [°C]	$122,5 \pm 0,1$	$132,2 \pm 0,1$

A higher degree of crystallinity means that there are more crystalline regimes with highly ordered lamellae, where the ability of the molecules to arrange themselves into crystals is hindered. The higher degree of crystallinity means greater mechanical properties, which is very important in bearing application.

4. CONCLUSIONS

The aim of this work was to find out differences in structural parameters of UHMWPE in two material states – non-crosslinked (conventional) and crosslinked. Crosslinking is applied to polymeric elements of hip implants in order to make it more durable and stable in human body. The production process and sterilisation method have a great impact on final product properties. Choosing a material and a processing procedure the properties of UHMWPE acetabular cup can be somehow controlled.

Crosslinking has been introduced to UHMWPE implants in order to increase wear resistance so reducing the risk of implant malfunction. However, crosslinking leads to a decrease in some of the mechanical properties, such as ultimate tensile strength and resistance to fatigue crack propagation. Due to crosslinking, the degree of crystallinity of the material is reduced.

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