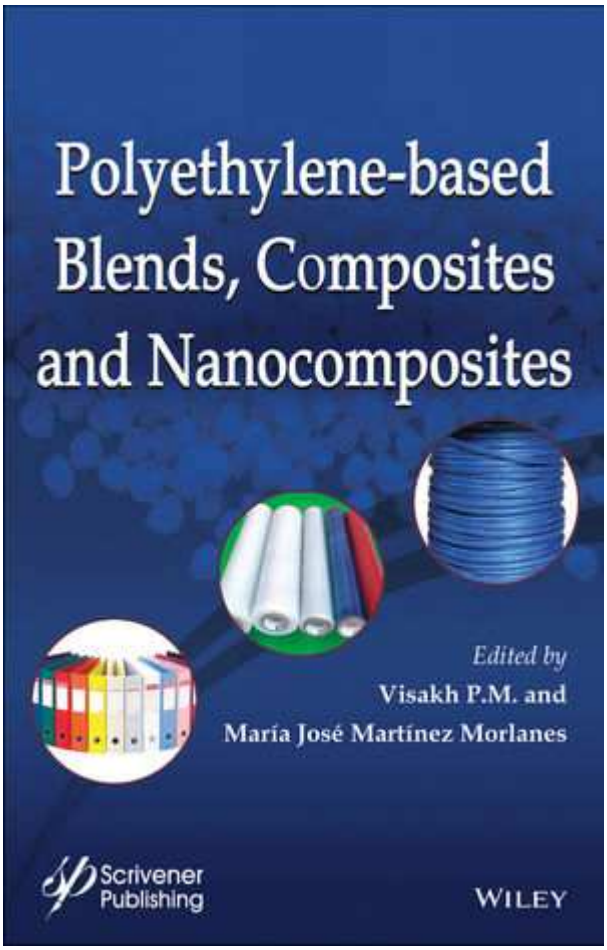

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Ultra High Molecular Weight Polyethylene and its Reinforcement with Carbon Nanotubes in Medical Devices

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Ultra high molecular weight polyethylene and its reinforcement with carbon nanotubes in medical devices

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Abstract

This chapter discusses the advantages and complexities of ultra high molecular weight polyethylene (UHMWPE) when used as a bearing material for total joint arthroplasty (TJA) and total knee arthroplasty (TKA). The UHMWPE internal structure and its mechanical response depend strongly on a diversity of factors that include radiation crosslinking, fiber reinforcement, and the addition of antioxidants such as Vitamin E or Vitamin C. All these manufacturing procedures induce morphological changes and simultaneously alter the mechanical properties of UHMWPE. The importance of UHMWPE on arthroplasty, including the advantages, the limitations and the strategies devised to overcome the known drawbacks are discussed in the first section. The following sections revise and discuss the biocompatibility, the manufacturing processes, the tribological behaviour, the aging by oxidation and irradiation of UHMWPE and UHMWPE-CNT nanocomposites. The last section analyses the viscoelastic behavior of UHMWPE and its implications on the long-term survival of total joint arthroplasty.

Keywords: ultra high molecular weight polyethylene, arthroplasty, orthopedic implants, biocompatibility, wear, oxidation, irradiation, cross-linking, viscoelastic, viscoplastic, carbon nanotubes

1. Introduction

The widespread use of ultrahigh molecular weight polyethylene (UHMWPE) in orthopedic implants as a bearing element is a relevant example of its importance in medical devices [Gomez-Barrena08]. There are several types of polyethylene with different molecular weight and internal chain arrangements. While high density polyethylene (HDPE) has a molecular weight of up to $2x10^5$ g/mol, UHMWPE has a molecular weight up to $7.5x10^6$ g/mol, i.e. one order more than that of HDPE (Kurtz [2009a]). Owing to such high molecular weight, the ultimate strength and impact strength of UHMWPE are also observed to be higher. Yet, the most appropriate characteristics of the UHMWPE, when used as a bearing component in orthopedic implants, are its higher wear resistance. In spite of that the wear of UHMWPE in the form of microscopic particles led to osteolysis and later to the loosening of the implant

which catalyzed its failure on the long-term (Kurtz [1999a]). In short, there has been always a continued interest to further enhance the wear resistance of UHMWPE.

The most representative group of orthopedic devices using UHMWPE as a bearing material is the total joint arthroplasty (TJA). The most important are the total hip arthroplasty (THA) and total knee arthroplasty (TKA) (Kurtz [2009a]) that are described schematically in Figure 1. In USA, according to the estimation provided by Kurtz [2009e], the number of primary TKA and the number of primary THA were around 700,000 and 300,000, respectively in 2010. The increasing impact on the population healthcare may be given by some projections for next 20 years. It is expected an increase in demand for primary THA and TKA surgical operations by 174% and 673% respectively, (Kurtz [2007]). Concurrently, the number of TJA revisions raised steadily in USA since 1993. In 2010, the number of TKA and THA revisions was around 60,000 and 45,000, respectively (Kurtz [2009e]).

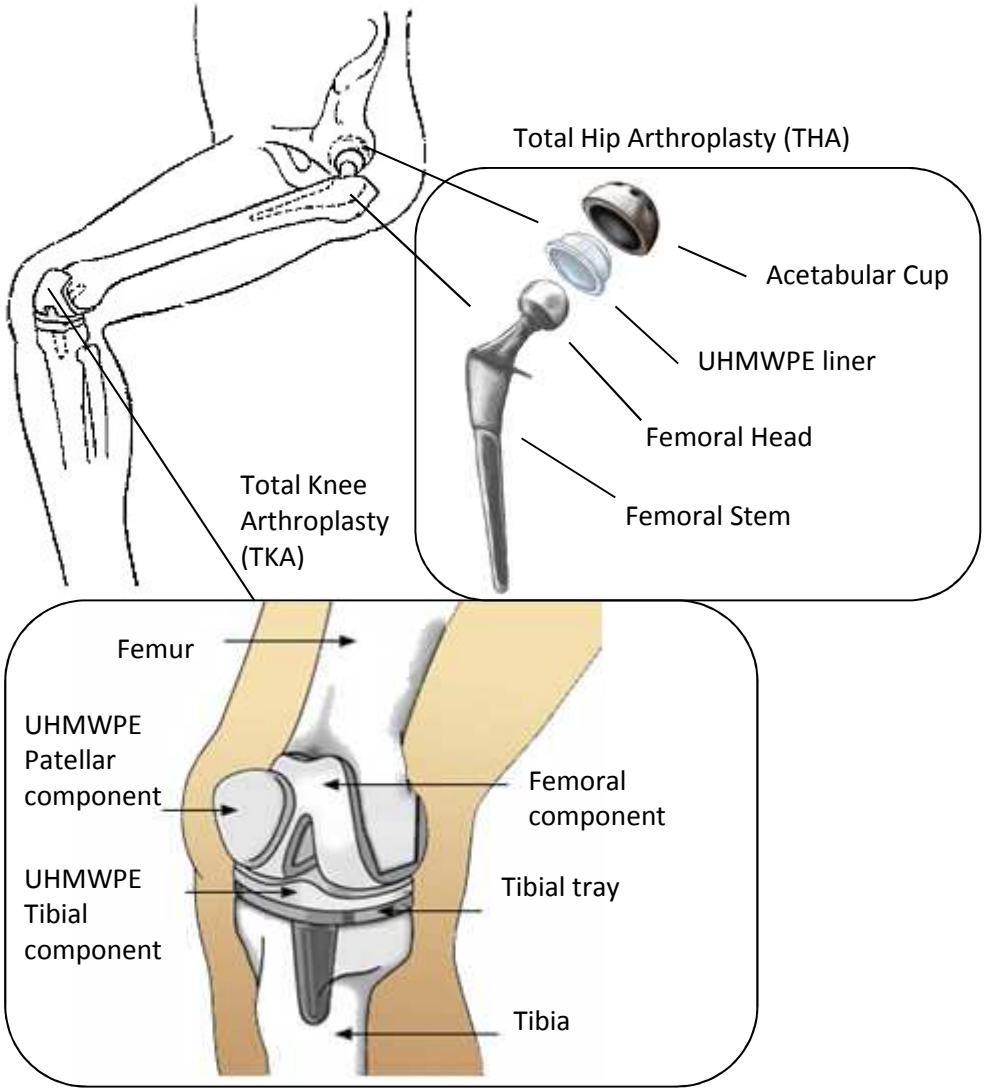

Figure 1: Schematic representation of total joint arthroplasty (TJA) using UHMWPE as bearing element.

Any improvement on durability of the orthopedic implants must rely on a good knowledge of the various factors affecting the wear behavior of the UHMWPE components. According to studies conducted on *in vitro* simulators, wear is dependent on kinematics of the articulating surfaces, the prosthesis design and the type of material (McEwen [2005]). Improvements on these simulators are still being proposed to provide clinically relevant testing conditions (Chyr [2013]). Numerical simulation is a cheaper alternative to study the wear behaviour of UHMWPE components, which can provide relevant information (Cho [2004], Fialho [2007], Teoh [2002], Bevill [2005]). In this context, the constitutive equations are necessary to calculate the stress and strain under prescribed boundary and loading conditions. UHMWPE has a viscoelastic nature, as

any polymer, that can be described by simple models (Deng [2010], Guedes [2011a]). Mechanical behavior of UHMWPE was also measured and described mathematically in the large strain range (Bergström [2004]).

The purpose of this chapter is to review the state-of-the-art and expose the complexities of UHMWPE used as a bearing material in TJA and TKA. In this context, the UHMWPE displays a diversity that includes radiation crosslinking, fiber reinforcement, and addition of antioxidants such as Vitamin E or Vitamin C. These techniques induce morphological changes and simultaneously alter the mechanical properties of UHMWPE. The next section describes the importance of UHMWPE on arthroplasty, including the advantages, limitations and the strategies devised to overcome the known drawbacks. The biocompatibility, the manufacturing processes, the tribological behaviour, the aging by oxidation and irradiation of UHMWPE and UHMWPE-CNT nanocomposites are reviewed and discussed in the following sections. The last section is devoted to analyze the viscoelastic behavior of UHMWPE.

2. UHMWPE for total joint arthroplasty

UHMWPE has been used since 1960s as a successful biomaterial for use in hip by Sir John Charnley, knee by Frank Guston, and more recently for spine implants (Kurtz [2009a]). For public consultation, there is an online repository of information and review articles on UHMWPE used in total joint replacements [UHMWPE Lexicon, http://www.uhmwpe.org]. Historical data for primary TJA in the USA during 1993 and 2006 revealed a steady exponential growth. In 1993, the number of primary TKA was around 200,000 against 140,000 for primary THA. While in 2006, the number of primary TKA performed rose to about 520,000 against 240,000 for primary THA. It is noted that an increase of total knee and total hip replacements was observed to be 160% and 70%, respectively (Kurtz [2009a]). Extrapolations made for 2030 expected an increase of primary THA and TKA procedures by 174% and 673% respectively, (Kurtz [2007]).

An attempt to improve the performance of UHMWPE started almost immediately after its introduction as a bearing material in orthopedic devices. The motivation was the

wear debris related osteolysis that was the main cause of failure in joint replacements based on UHMWPE inserts (Brach del Prever [2009]). Thus, it was expected that any improvement on wear resistance of UHMWPE is expected to increase the life of an implant leading to defer the TJA revision.

One of the early approaches to improve the wear resistance was based on carbon fibre reinforced UHMWPE composites. The commercial version designated as Poly II was attempted clinically in 1977 (Kurtz [2009a]). However, clinical use of Poly II resulted wear, fracture and delamination under *in vivo* condition leading to its withdrawal from the market (Kurtz [2009a]). Moreover, it was observed that the high interfacial stress and the poor *fiber-matrix* adhesion led to fiber-matrix delamination failure, which impaired the composite performance in tension (Birken [1998]). This phenomenon was also responsible for a much higher fatigue crack growth compared to the unreinforced UHMWPE (Connelly [1984]). As reported by Steven Kurtz [2009c], in spite of these complications some of the implanted components of carbon fibre reinforced UHMWPE survived more than 30 years. It is expected that the analysis of those long-term retrieved bearings would contribute to revisit these composites (Kurtz [2009c]).

The clinical introduction of a highly crosslinked, irradiated and thermal treated UHMWPE (HXLPE) in the late 1990s provided a significant improvement on the wear resistance of UHMWPE. These materials are processed with high-energy irradiation with a total dose ranging from 60 to 100 kGy (Brach del Prever [2009]). Though the wear resistance of UHMWPE was increased significantly, its mechanical properties were observed to be decreased (Kurtz [2009a]). The high-energy irradiation led to chain scission and the formation of free radicals, which caused the degradation of mechanical, chemical and physical properties of the polymer(Costa [2009a]). In the presence of Oxygen, the oxidative degradation (oxidation) occurred, which can't be interrupted once it is initiated. The rate of oxidation increased continuously with a series of reactions that involve free radicals and Oxygen (Brach del Prever [2009]). In order to avoid the same, UHMWPE is thermally treated to remove the residual radicals. By this way, radiation related oxidative degradation process is largely prevented (Brach del Prever [2009]). However, depending on the manufacturer, there are two types of thermal processing by: annealing (below melt transition temperature 137ºC) and re-melting (above melt transition temperature). Although the later is the only process to assure a complete elimination of the residual free radicals formed during radiation, it

reduces the material properties significantly than the annealing process (Kurtz [2002]). This is related with the crystallinity degree which is higher for the annealed material. The general route used for production of the first generation HXLPE material involves 3 steps: irradiation crosslinking, thermal treatment to prevent oxidative degradation and sterilization (Kurtz [2009a]). Each manufacturer is proprietor of a combination of these steps, for a particular HXLPE material. The expansion of crosslinking technology into total THA and TKA procedures originated numerous proprietary HXLPE, some are available for hips and others exclusively for knees. Fewer HXLPE can be found in both hip and knee products..

After 2005, a second generation of HXLPE materials has been introduced. These materials were developed to eliminate the shortcomings of the first-generation HXLPE by reducing the potential for material oxidation in the long term while preserving the bulk mechanical properties (Kurtz [2009a]).

One of these second generation HXLPE contains a biocompatible and nontoxic antioxidant, alpha-tocopherol (vitamin E), which is added to stabilize the irradiated crosslinked UHMWPE (Brach del Prever [1994, 2009]). Thus, vitamin E provides oxidation resistance by absorbing the residual free radicals, which avoids the post-irradiation melting treatment (Kurtz [2009a]). Clinical data regarding the performance of these formulations is becoming available after the first decade of clinical use (Kurtz [2011]). Although it is clear that the wear resistance of blend has been improved when compared against the conventional UHMWPE, uncertainty was raised about the long-term survival of HXLPE, which is related to the oxidation in the edge of annealed liners and cracks in re-melted liners detected during this period of time. Another decade will be necessary to have an answer on how these factors would affect the long-term survival of TJAs.

Many manufacturers are now developing HXLPE materials containing vitamin E. There are two different processes to add vitamin E either during moulding/ extrusion before irradiation or by diffusion after irradiation (Brach del Prever [2009]). Since the presence of vitamin E in UHMWPE during irradiation reduces the efficiency of crosslinking, the diffusion after irradiation process appeared to be a better approach. Yet, it is difficult to control the concentration and the distribution of the alpha-tocopherol during the diffusion process. Although the inclusion of vitamin E seems to be a promising

evolution step, it does not suppress totally the oxidation caused by the high-energy radiation (Brach del Prever [2009]). *In vitro* and animal studies confirmed the biocompatibility of vitamin E-stabilized UHMWPE (Bracco [2011]). However, clinical data regarding the performance of these formulations is still under way (Kurtz [2011]). Ascorbic acid (vitamin C) is an alternative additive for inhibiting the oxidation of UHMWPE. The antioxidant effectiveness of ascorbic acid is well known and it proved to be effective in reducing the oxidation of UHMWPE (Rocha [2010]).

HXLPE materials available in the market are summarized in Figure 2.

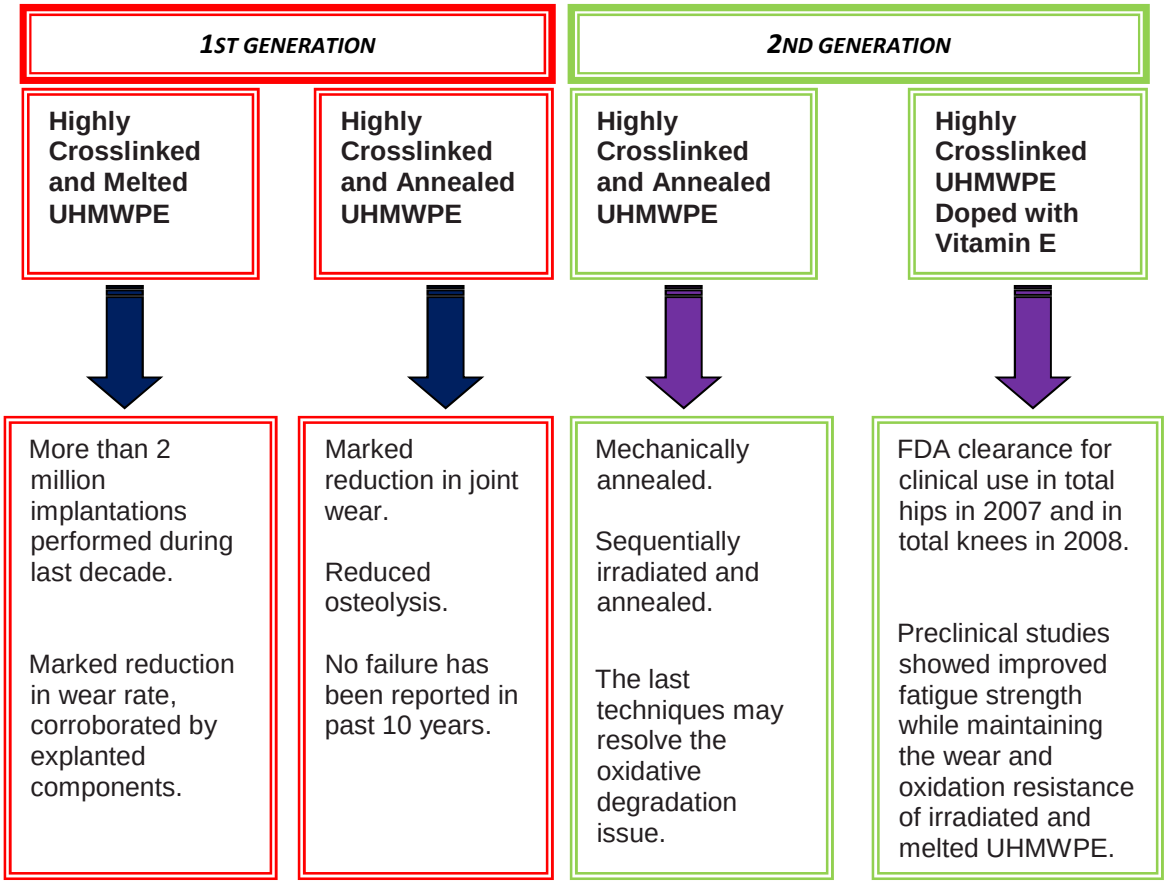

Figure 2: HXLPE material available for TKA and THA.

More recently, UHMWPE nanocomposites possessing higher mechanical performance and wear resistance have been proposed as an alternative material. Sreekanth et al. [2013a] verified that UHMWPE reinforced with multi walled carbon nanotubes (MWCNTs) has good biocompatible characteristics, comparable to plain UHMWPE. Zoo et al. [2004] reported that the wear resistance of UHMWPE was significantly

increased when MWCNTs were added up to 5 wt%. In another study by Martínez-Morlanes [2012], it was verified that when the MWCNTs concentration was increased, the number of free radicals generated by the gamma irradiation process was decreased. Conjointly to increase of the oxidative resistance, the efficiency of the crosslinking density of UHMWPE was maintained by the reinforcement of MWCNTs, unlike vitamin E that inhibits radiation crosslinking.

3. Biocompatibility of CNTs and UHMWPE-CNT nanocomposites

Even though UHMWPE is biocompatible in its bulk form, the polymer wear debris can cause osteolysis in surrounding tissues, leading to bone resorption and implant loosing and can leave to a revision surgery for an implant replacement which can be painful for the patient (Dumbleton [2002]). Different studies revealed that the wear particles generated by different grades of polyethylene can play a different role in the biological reactions (Tipper [2000]). Polyethylene having different molecular weight, level of crosslinking and even hydrophobic/hydrophilic properties is expected to generate wear particles with diverse biological response. It is well known that the incorporation of CNTs into a polymeric matrix can enhance its mechanical properties along with a possible decrease on the size and generation of wear debris. However, the biocompatibility issues of the CNTs with the human cells are still having the high controversy related to such field. As the CNTs are in the order of few nanometers, it makes this issue particularly sensitive, since it is not clear the interaction effects of such carbon-like nanoparticle with the living tissues.

Some authors described strong cytotoxic effects on guinea pig alveolar macrophages of single walled carbon nanotubes (SWCNTs) and, at a smaller extent, of multi walled carbon nanotubes (CNTs), when compared with fullerenes (C_{60}) (Jia [2005]). Magrez et al [2006] conducted some experiments on three lung-tumor cell lines and the results suggested that CNTs led to proliferation inhibition and cell death, although CNTs presented less toxicity than carbon black nanoparticles and carbon nanofibers. A study conducted by Sharma et al. [2007] concluded that the SWCNTs induced oxidative stress in rat lung cells. Muller et al [2005] compared asbestos, carbon black and CNTs effects when instilled in the trachea of rats at different doses. They described dose-dependent

persistent inflammation and granuloma formation, which are more significant with CNTs than the carbon black but less extensive than the asbestos. Ryman-Rasmussen et al [2009] described the inhaled CNTs migration to the subpleura and associated increased number of pleural mononuclear cells and subpleural fibrosis, further advising caution and appropriate security measures when handling with CNTs. Zhu et al [2007] observed that the CNTs could accumulate and induce apoptosis in mouse embryonic stem cells, and they increased the mutation frequency of them compared to spontaneous mutation, suggesting careful scrutiny of the genotoxicity of the nanomaterial. It was demonstrated for other types of nanoparticles that the nanoparticles might reach the central nervous system (CNS) following their inhalation (Elder [2006]). CNTs induction inflammatory pathways may be similar to those of combustion-derived metals (Ding [2005]) and cause decreased cell viability, changes on metabolic, cell signaling, stress and cytoskeletal protein expression (Witzmann [2006]). Bottini et al. [2006] compared the effect of pristine and oxidized CNTs on human-T lymphocytes and described increased toxicity of oxidized CNTs with high doses, even if oxidation increased solubility. Brown et al [2007] suggested from their *in vitro* studies that the response of monocytic cell is strongly dependent of morphology and state of aggregation of the CNTs. Long, straight well-dispersed nanofilaments induced the production of more TNF-alfa and ROS than the highly curved and entangled aggregates; incomplete uptake or frustrated phagocytosis of CNTs was also described. Barillet et al [2009] showed that the short (0,1-5nm) and long (0.1-20nm) CNTs and the presence of metal residues induced different cell response and toxicity. Nevertheless, the results of an *in vitro* studies by Simões et al [2010] showed the response of human osteoblast-like MG63 cells after 6 days in culture in contact with particles artificially generated from pure UHMWPE and nanocomposites of UHMWPE/CNTs with 0.2 wt % of CNTs (Table 1), which indicated good cytocompatibility of CNTs, similar to that of conventional UHMWPE, and it is suggesting its potential to use in orthopaedic applications. Moreover, it was also observed a decreasing trend of the wear coefficient with an increase of CNTs concentration in the polymer confirming the same trend of wear volume. It was attributed to the enhanced interfacial strength between the polymer and the CNTs resulting in a good load transfer effect to the CNTs from the polymer (Kanagaraj [2007], Kanagaraj [2010]). The results gathered by Kanagaraj et al [2010] have shown that the wear resistance of UHMWPE was significantly improved with the addition of CNTs by wear volume and wear coefficient were decreased with an increase

of CNT loading (Fig. 3). The results reveal the high potential for CNTs to be used in medical applications, namely hip implants.

Table 1- Total protein (24 wells) and interleukin-6 (IL-6, 12 wells) measurements in MG63 cells, seeded at an initial concentration of 7600 cell/well. From (Simões [2010]).

	Total protein (µh/mL)	IL-6 (pg/mL)
Control	139.73 ± 10.78	90.93 ± 10.30
UHMWPE	137.07 ± 6.17	92.52 ± 11.02
MWCNT/UHMWPE	163.29 ± 11.81	108.99 ± 9.90

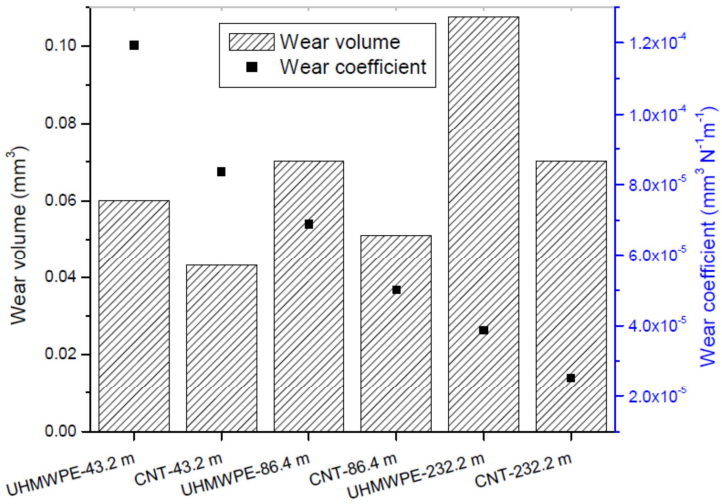

Fig. 3 - Variation of wear volume and wear coefficient of UHMWPE and composite against sliding distance. From (Kanagaraj [2010]).

4. Manufacturing processes of UHMWPE-CNT nanocomposites

The incorporation of CNTs into a polymeric matrix, such as UHMWPE is quite difficult due to strong Van der Waals forces which tend to clump the CNTs together leading to poor distribution of the CNTs into the polymeric matrix. To promote the disentanglement of the CNTs and hence a better dispersion within the UHMWPE matrix, functionalization techniques must be envisaged when preparing the nanoparticles prior to their incorporation in the polymer.

4.1. CNTs functionalization

The functionalization methods can be divided into two main techniques: chemical (covalent) and physical (noncovalent) functionalization as interactions between active materials and CNTs. Fig. 4 shows the schematic diagram of the functionalization possibilities for CNTs (Hirsch [2002]).

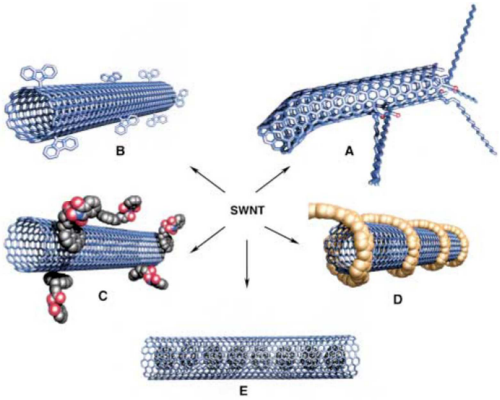

Fig. 4 – Functionalization possibilities for SWNT: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C_{60}. For methods B-E, the tubes drawn in idealized fashion, but defects are found in real situations. From (Hirsch [2002]).

Covalent Functionalization

Chemical functionalization is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at the terminal ends of the CNTs or at their sidewalls (Ma [2010]). Direct covalent sidewall functionalization is associated with a change on hybridization from sp^2 to sp^3, and simultaneously, a loss of π-conjunction system of graphene layer (Fig. 4A). This process can be made by reaction with some molecules of a high chemical reactivity. The defects functionalization of CNTs is another method for covalent functionalization. This method takes advantage of chemical transformation of defects cites on CNTs (Fig. 4B). The defects created on CNTs by oxidants are stabilized by bonding with carboxylic acid (-COOH) and hydroxyl (-OH) groups. The CNTs functionalized through this method are soluble in many organic solvents because the hydrophobic nature of the CNTs has been changed to hydrophilic due to the attachment of polar groups. As an example, the present authors performed covalent functionalization with nitride and sulphuric acids in a proportion of (1:3) and

the results have shown that CNTs maintain its physical integrity and that they are no longer entangled as previously to chemical treatment (Fig. 5 and Fig. 6).

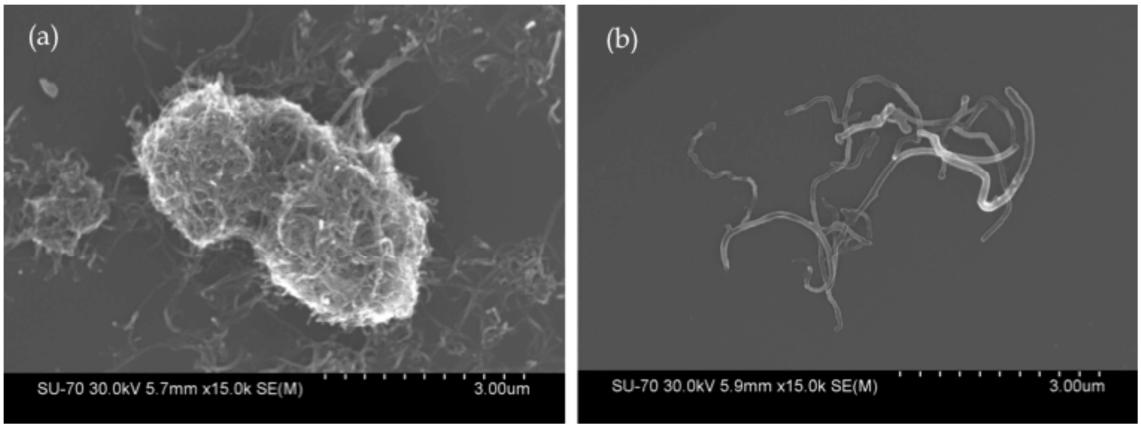

Fig. 5 - Scanning electron microscopy of the (a) non-treated CNTs and (b) chemically treated CNTs. From (Oliveira [2012]).

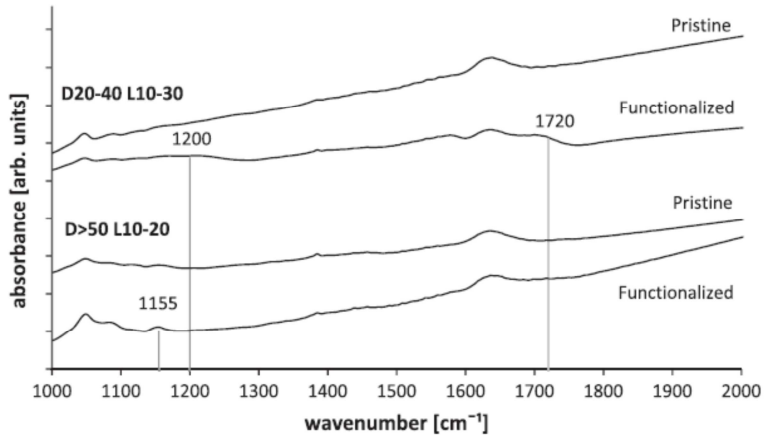

Fig. 6 - Fourier Transform Infrared Spectroscopy (FTIR) spectra of pristine and functionalized CNTs. From (Lamas [2012]).

Chemical functionalization can produce strong interfacial bonds of the CNTs with many polymers, allowing nanocomposites with embedded CNTs to detain higher mechanical and functional properties.

However, chemical functionalization can have essentially two major drawbacks: 1. during functionalization reaction, especially those that use ultrasonication process, can cause large defects on the sidewalls of CNTs and can cause fragmentation of the CNTs into smaller pieces; and 2. normally these processes used concentrated acids or strong oxidants, which are environmentally unfriendly.

Non-covalent functionalization

The huge advantage related to physical functionalization is that it does not destroy the conjugated systems of the CNTs sidewalls, and therefore it does not affect the final structural properties of the material. Non-covalent functionalization is an alternative method for tuning the interfacial properties of the CNTs.

The CNTs can be functionalized noncovalently by different paths, as aromatic compounds, such as pyrene, porphyrin; surfactants, and polymers (Zhao [2009]). The suspension of CNTs in the presence of polymers leads to the wrapping of polymer around the CNTs to form supermolecular complexes of CNTs. The polymer wrapping process is achieved through the Van der Waals forces interactions and π-π stacking between CNTs and polymer chains containing aromatic rings (Fig. 7A) (Ma [2010]). The use of surfactants and its effects on dispersibility of CNTs has been studied. The surfactants studied included: non-ionic (Fig. 7B)) (Geng [2008]);anionic; and cationic. The physical adsorption of surfactant on the CNTs surface lowered the surface tension of the CNTs, preventing the formation of aggregates, and overcoming the Van der Waals attraction by electrostatic/steric repulsive forces. The efficiency of this method depends strongly on the surfactant properties, the chemistry medium and on the polymer matrix. In Table 2,Ma, et al [2010] summarizes the main advantages and disadvantages of various CNTs functionalization methods.

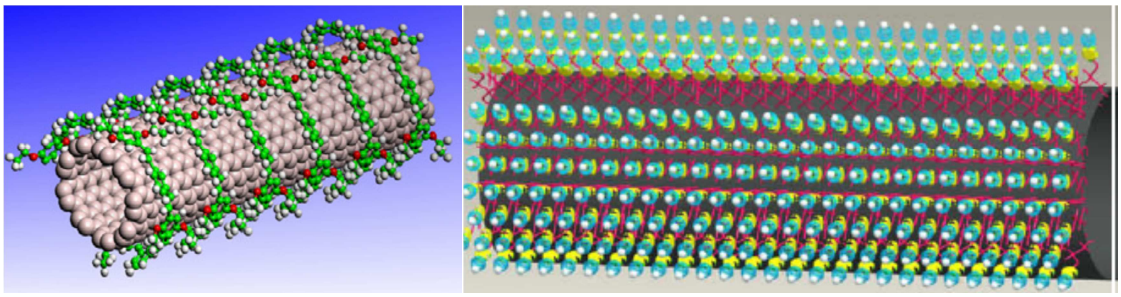

Fig. 7 - Schematic of CNT functionalization using the noncovalent methods, A) Polymer wrapping; B) surfactant adsorption. From (Ma [2010], Geng [2008]).

Table 2 - Advantages and disadvantages of various CNTs functionalization methods. From (Ma [2010])

Method		**Principle**	**Possible damage to CNTs**	**Easy to use**	**Interaction with polymer matrix**	**Re-agglomeration of CNTs in matrix**
Chemical method	Side wall	Hybridization of C atoms from sp^2 to sp^3	✓	×	S	✓
	Defect	Defect transformation	✓	✓	S	✓
Physical method	Polymer wrapping	Van der Waals force, π-π stacking	×	✓	V	×
	Surfactant adsorption	Physical adsorption	×	✓	W	×
	Endohedral method	Capillary effect	×	×	W	✓

4.2. Processing UHMWPE-CNTs

There are several processing methods available to manufacture polymer/CNTs nanocomposites. It may be considered essentially three methods to incorporate CNTs into polymeric matrices: 1) solution mixing or film casting of suspensions of CNTs in soluble polymers; 2) in situ polymerization of CNT-monomer polymer mixture and 3) melt mechanical mixing of CNTs with polymer.

Solution mixing

The most used technique to incorporate CNTs into polymeric matrices is composed of the mixture of both components into a certain solvent and evaporates the latter to form a composite film. This method consists of three steps: dispersion of CNTs into a suitable solvent; mixing with the polymer previously dissolved in the same solvent and recovery of the nanocomposite by precipitating or casting a film. The mixture of CNTs into the solvent can be performed by magnetic stirring, shear mixing, reflux or ultrasonication.

The use of ultrasonication with high energy and for a long time can shorten the nanotubes length, i.e., reduces its aspect ratio. In this case the use of surfactants can be useful; however its use can deteriorate the transport properties of the nanocomposites because the surfactant remains in the final nanocomposite. Ruan et al [2003] processed UHMWPE/CNT through solution casting and obtained an increase in the ductility. Wang et al [2005] prepared UHMWPE fibers reinforced with CNTs through gel spinning, and reported a small increase in the tensile modulus and strength for CNTs concentrations of 3wt%. Bin et al [2003] prepared UHMWPE/CNT films by solution casting by dispersing the CNTs in O-Xylene by magnetic stirring and untrasonication, then the mixture was poured into the UHMWPE-Xylene solution and refluxed for 1h.

In situ polymerization

The main advantage of this method is that it enables grafting of the polymer macromolecules onto the sidewall of the CNTs. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution casting or melt mechanical mixing. *In situ* polymerization can be applied for preparation of almost any CNT-polymer nanocomposite, which can be non-covalently or covalently bound to polymer matrix. Kaminsky et al [2007] prepared UHMWPE/CNTs nanocomposites by *in-situ* polymerization using metallocene, and investigated the influence of the CNT concentration in the thermal properties. Sanches et al [2009] produced UHMWPE/CNTs nanocomposites via *in situ* polymerization by a $TpTiCl_2(Et)$ system, and investigated the effect of CNTs concentration on the activation of the catalyst. Amoli et al [2012] prepared nanocomposites of UHMWPE/CNT through a bi-supported Ziegler-Natta catalyst system, and evaluated the mechanical properties of the prepared nanocomposites. The results revealed an enhancement of the Young's modulus, yield stress and ultimate tensile strength. Recently, Park et al [2013] prepared UHMWPE/CNT nanocomposites by *in situ* polymerization using Ti-based Ziegler-Natta catalysts fixed on the surface of CNTs, and have obtained very good dispersion of CNTs into UHMWPE matrix. They have also shown that the composites prepared through *in situ* polymerization detain superior mechanical properties to those prepared by mechanical melt mixing.

Melt mechanical mixing

The melt mechanical mixing is the preferable choice for industrial applications, due to its low cost and simplicity to facilitate large scale production for commercial applications. In a simple way, the melt processing consists of the melting of the polymer pellets to form a viscous liquid and application of high shear forces to disperse the CNTs. However, high shear forces and high temperatures can cause damages on the nanocomposite properties. It is detrimental to determine a compromise between the shear force and temperature, in order to obtain a homogeneous distribution of the CNTs into a polymeric matrix, without losing the required nanocomposites properties. Xue et al [2006] prepared UHMWPE-20wt%HDPE and UHMWPE-HDPE-CNT blends by mixing the melt in a kneader and then hot-pressed into plates. They reported an increase in the yield strength with the addition of 2 wt% of CNTs. Ruan et al [2006] also reported the fabrication of UHMWPE/CNTs with properties close to the commercially available fibers like Kevlar. Bakshi et al [2007] used a quite different technique to prepare films of UHMWPE/CNTs. They have prepared these films by electrostatic spraying of the milled UHMWPE/CNTs into a Teflon sheet, and then cured it in an oven for consolidating the powder into a film. The results revealed an enhancement on the Young's modulus and a decrease on the stress to fail with the addition of 5% CNTs. Kanagaraj et al [2011] prepared nanocomposites of UHMWPE/CNTs through a variation of the melt mechanical processing technique. The latter used the mechanical ball-milling to mix the raw UHMWPE with CNTs, and after that the powder composite was processed by compression moulding in a hot press. The results have shown a homogeneous distribution of the CNTs into the UHMWPE (before and after processing), and an enhancement of the overall mechanical properties.

5. Tribological behaviour of UHMWPE and UHMWPE-CNT nanocomposites

Reinforcing UHMWPE with different filler particles has been an alternative to crosslinking technique to improve its wear resistance. The most direct advantage of using filler particles over crosslinking is to avoid the free radical generation and accelerated oxidation, Schwartz et al. [2007]. In order to improve some of the specific mechanical properties, UHMWPE is also often reported to be filled with diverse inorganic filler particles. However, the selection of a particular reinforcing material used

to prepare the composites is based on the requirement of the final product in biomedical application. The improvement of wear resistance with the use of fillers in various polymers has been widely reported. . The article of Iijima et al. [1991] has triggered thoughts of multifarious researchers to investigate the potential use of carbon nanotubes as a reinforcing element for polymer nanocomposites due to their remarkable properties such as extremely high Young's modulus and tensile strength, Treacy et al. [1996]. Though MWCNTs are being considered in different applications, medical science is one of the fields where they are explored to be used as a reinforcing material with UHMWPE in order to improve its longevity. Based on the studies reported on the enhancement of mechanical properties of UHMWPE, multi walled carbon nanotubes (MWCNTs) seem to be promising reinforcement material, (Ruan et al. [2003], Xue et al. [2006], Bakshi et al. [2007, 2007a], Morlanes et al. [2011], Samad et al. [2011, 2011a], Maksimkin et al. [2012], and Sreekanth et al. [2013b]). However, very few studies were reported detailing the influence of MWCNTs on the wear performance of UHMWPE. The following discussion contains two sections (i) tribological behaviour of UHMWPE (ii) Tribological behaviour of UHMWPE/ MWCNTs composites. A conclusion note on the scope of future research has also been deliberated at the end of the section.

5.1 Tribological behaviour of UHMWPE

UHMWPE is used as an articulating surface in both hip and knee joint replacements. As an acetabular component in THR (total hip replacement), its annual wear rate was reported to be approximately 0.1 mm/year or 80 mm^3/year against a 32 mm diameter femoral head, Hall et al. [1996], and Oonishi et al. [1998]. It is approximately a 30-fold reduction in wear rate in comparison with a PTFE socket that was first introduced by Dr.Charnley, Wang [2001]. The accumulated wear debris led to adverse tissue reactions, which results in bone absorbtion or osteolysis. Thus, it is essential to reduce the wear debris generated by UHMWPE. It can be achieved by thorough understanding of the different factors and identification of prominent wear mechanisms for the generation of such wear debris in UHMWPE. An attempt has been made in order to understand the wear behaviour of virgin UHMWPE using different wear simulators and different testing conditions. The wear of UHMWPE acetabular component depends on the (i) geometrical factors (head diameter, surface roughness) (ii) test conditions (type

of lubricant, simulator, counterface material, *in vivo*, *in vitro* etc.) and (iii) manufacturing process (extruded, compression moulded, moulding pressure, atmosphere etc.).

Dowson et al. [1987] investigated the influence of counterface imperfections on UHMWPE using a linear reciprocating wear tester. It was reported that the imperfections in stainless steel counterface were in the form of transverse/longitudinal scratches or single indentations. It was found that a transverse scratch on the counterface increased the wear rate considerably by piling up steel along the edge of the scratch, whereas the longitudinal scratches yielded a comparatively less wear rate of the polyethylene and the indentations were reported to have shown a little effect upon wear rate. Their findings demonstrated that simple imperfections on a hard counterface can have tremendous influence on the wear of polymers. Wang et al. [1998] studied the effect of femoral head surface roughness on the wear of UHMWPE acetabular cups using a hip joint simulator and a reciprocating wear tester, and reported that the reciprocating wear tester severely exaggerated the effect of counterface roughness compared to that of hip simulator. The authors concluded that the wear tester overestimated the wear rate of the UHMWPE even against smooth undamaged counterfaces. Therefore, it is understood that the clinical variation of wear cannot be fully explained by variation in wear performed on conventional wear testers. Watters et al. [2005] performed wear studies on UHMWPE on a hip simulator and confirmed the influence of femoral head surface conditions on the wear behaviour of UHMWPE. Livermore et al. [1990] examined 385 hips after 9.5 years of replacement and reported that the least amount of linear wear was associated with the use of a 28 mm diameter femoral head and the higher rate of linear wear was observed with 22 mm head. It was suggested that there was an association between the amount of wear debris and the femoral head diameter. Wang et al. [1996] investigated the size and morphology of wear debris produced by a hip joint simulator with bovine serum and water as lubricants. It was reported from the bovine serum lubricant that the wear debris was submicron size and elongated shape and, in addition, the formation of transfer film was also observed on the femoral heads. In case of water lubrication, the large flakes of UHMWPE about 2-3 mm were produced along with transfer films on the femoral heads. Wang et al. [1995] studied the different wear mechanisms exhibited by UHMWPE. It was reported that the wear occurred due to both microscopic (ripple formation and plastic deformation) and macroscopic processes (cracking and

delamination). Wear initiates with microscopic process and transits into macroscopic process, and the transition between these two wear processes primarily depends on the mechanical properties of UHMWPE. They concluded that the wear resistance of UHMWPE can be improved by increasing its ultimate tensile strength and ductility. Karuppiah et al. [2008] reported that UHMWPE exhibited lower frictional force, increased scratch resistance, surface hardness and crystallinity. Reports on reciprocating wear tester have also shown a reduction of both microscale and nanoscale wear. Wilches et al. [2008] compared the influence of counterface material on the wear of UHMWPE. Stainless steel 316L and Titanium alloy were used as a counterface material under bovine serum lubrication. Polymer adhesion to the metallic surfaces and subsequent failure of subsurface were the common wear mechanisms that were observed irrespective of the counterface. The authors also reported that the formation of transfer film reduced the coefficient of friction. It was concluded that the Titanium alloy offered better wear and corrosion resistance than the stainless steel under same working conditions. Parasnis et al. [1998] studied the effect of consolidation pressure on the properties of UHMWPE and reported that UHMWPE exhibited superior mechanical and tribological characteristics at a consolidation pressure of 15 MPa. However, Gul et al. [2003] reported that the consolidation temperature has very little influence on both the adhesive and abrasive wear of UHMWPE. Several other studies were also reported, which extricated the influence of wear mechanisms by geometric, manufacturing processes on UHMWPE. Nevertheless, the trend exhibited by UHMWPE remained the same except the variation of severity/intensity of the wear phenomena.

Has the above discussion, it is understood that wear of UHMWPE primarily occurred due to adhesive, abrasive, subsurface cracks and delamination. These wear phenomena were affected by several factors, which are not inherent material properties of the articulating surface. A reduction of wear volume is always desirable to increase the longevity of the bearing surface. It was attempted by using various fillers as reinforcing materials in UHMWPE. Although a wide variety of fillers was used, MWCNTs were chosen for discussion in the present chapter in relevance to their superior properties. A detailed discussion on the influence of MWCNTs on the tribological behaviour of UHMWPE has been presented in the next section.

5.2 Tribological behaviour of UHMWPE/ MWCNTs composites

MWCNTs are the rolled graphene sheets, and thus they detain certain properties similar to that of graphene, which acts as a good solid lubricant. MWCNTs also exhibit lubricant characteristics, in addition to their superior mechanical properties. However, many studies have not reported the influence of MWCNTs on the wear behavior of UHMWPE. It is observed from the literature that the presence of MWCNTs could significantly reduce the wear of UHMWPE and thereby increase its longevity as a bearing surface.

Dangsheng (2005) studied the friction and wear behaviour of UHMWPE reinforced with carbon fiber using a block-on-ring wear tester. It was reported that the hardness of UHMWPE was increased by 91 % and the wear volume was reduced by 69 % at 30 wt. % of carbon fiber reinforcement under dry sliding condition. Though, adhesion, ploughing, plastic deformation and fatigue are reported to be primary wear mechanisms, the surface of pure UHMWPE under dry sliding condition exhibited severe microscopic undulations, which were minimized in case of carbon fiber reinforced UHMWPE composite, where only abrasive wear mechanism was dominantly observed. In addition, it was also ascertained that the wettability of the composites was greatly improved due to which the coefficient of friction of carbon fiber reinforced UHMWPE composites was very much lower than that of pure UHMWPE under distilled water lubrication conditions. Xue et al. (2006) reported the wear and creep resistance of a composite material consisting of UHMWPE and high density polyethylene (HDPE) polymer blend reinforced by MWCNTs. It was observed that the addition of 0.5 wt. % MWCNTs caused about 50 % reduction of the wear rate of UHMWPE-HDPE blend, which showed a better wear resistance than the pure UHMWPE and its blend. They also reported that the plastic flow was more prominent in UHMWPE/HDPE blends than the MWCNTs composites, whereas the formation of surface fatigue cracks was observed to be severe in composites. Kanagaraj et al. (2010) reported that the wear volume of UHMWPE was reduced by 34 % by reinforcing 0.2 wt. % MWCNTs over the sliding distance of 232 m. Due to less heat generation, the MWCNTs composites have shown better resistance to deformation and plastic flow. Zoo et al. [2004] reinforced UHMWPE with MWCNTs up to 0.5 wt. % and performed wear tests on a ball-on-disc wear test rig. The gravimetric analysis of wear revealed that the addition of 0.5 wt. % of MWCNTs reduced the wear of UHMWPE by 95 %, whereas, the morphology of the wear debris of composites and virgin UHMWPE did not vary significantly. The

coefficient of friction was increased as a function of MWCNTs concentration. The authors concluded that the enhancement of the friction coefficient and the reduction of wear loss were mainly due to the increase of the shear strength of the UHMWPE. Wei et al. [2006] investigated the tribological characteristics of UHMWPE/MWCNTs composites using a nanoindenter. It was reported that the depth of wear and the friction coefficient of UHMWPE were reduced with an increase of MWCNTs concentration and the respective reduction was found to be 40 and 13 % for 5 wt. % MWCNTs reinforced composite. The fracture crack generation and propagation in UHMWPE were also reported to be minimized due to addition of MWCNTs. It was ascertained that MWCNTs due to their large aspect ratio enhanced the chain mobility and thus altered the microstructure of the polymer leading to increased wear resistance of UHMWPE. However, their reports contradicted that of Zoo et al. [2004], where it was reported that MWCNTs did not alter the microstructure of UHMWPE. Nevertheless, in either of the reported studies, the presence of MWCNTs reduced the wear volume of polymer.

Campo et al. [2012] reinforced UHMWPE with 0.5 wt. % MWCNTs and performed wear studies on a pin-on-disc wear tester for 1 million cycles. It was reported that the wear loss of pure UHMWPE was 130 mg, which was increased to 178 mg (36 % higher) by reinforcing MWCNTs. It is noted that the presence of MWCNTs reduced the wear resistance of UHMWPE due to improper bonding between polymer and MWCNTs. Rhee et al. [2010] modified MWCNTs surface using two different techniques, oxidation and salinization, and then reinforced them with UHMWPE. Tribological tests at different sliding speeds (0.12, 0.18, and 0.24 m/s) were performed to understand the influence of surface groups on the wear resistance of UHMWPE. It was reported that the coefficient of friction was reduced by about 50 % in both oxidation and salinized techniques. However, the surface modification by oxidation was more effective in reducing the friction coefficient only for the lower sliding speed. Whereas, the salinized sample has a significantly lower friction coefficient than the raw and oxidized samples at all sliding speeds. The wear rate of UHMWPE at 0.24 m/s sliding speed was 2.6 mm^3/N-m, which was reduced by 42 and 70 % by oxidation and salinization processed MWCNTs in UHMWPE, respectively. It is indicated that the salinization technique allowed better dispersion and stronger interfacial bonding among the MWCNTs and the UHMWPE matrix compared to that of oxidation processed MWCNTs. Samad et al. [2011] coated UHMWPE reinforced with 0.1 wt. % of single-walled carbon nanotubes (SWCNTs) nanocomposite layer on a steel substrate and then

investigated its possibility as a boundary lubricant in bearings. It was reported that UHMWPE/MWCNTs coatings reduced the coefficient of friction by 35 % under dry sliding condition. It was also observed a superior scratch resistance as compared to that of DLC coatings. The presence of MWCNTs reduced the softening of the polymer coating and thus reduced the formation of scratches.

Based on the above discussion, it is understood that the presence of MWCNTs, in general, increased the wear resistance of UHMWPE. The wear mechanisms such as ploughing, abrasive wear, adhesive wear, surface and sub-surface cracking were found to be common in both UHMWPE and its composites, nonetheless, their severity was considerably reduced by introducing MWCNTs in UHMWPE. Exceptions were also reported, where the wear resistance was reduced with MWCNTs due to lack of surface modification. The type of surface modification on MWCNTs was also reported to have influenced the wear performance of UHMWPE. However, many unexplored research areas, such as influence of the aspect ratio of MWCNTs, oxidation and crystallinity of MWCNTs, surface modification by amine groups on the tribological behavior of UHMWPE are yet to be studied in detail. More to it, none of the studies reported so far have performed the tribological testing of the composites under body fluid conditions and hip simulators. As it is well known that the wear behaviour of composites tested on conventional wear testers deviated considerably from those performed on anatomical hip simulators, researchers should also focus on this area. Clearly, UHMWPE/MWCNTs composites are being investigated as a new potential alternative for orthopedic applications. However, due to the limited or no clinical experience of these composites in joint replacement, further research is required to be carried out in order to establish the biological consequences of these materials in clinical application.

6. Ageing of UHMWPE and UHMWPE-CNT nanocomposites

UHMWPE is a linear semi-crystalline polymer, composed of crystalline and amorphous phases. The typical crystallinity values are in the range of 45–60%. The crystalline phase contains chains folded into highly oriented lamellae. These lamellae are oriented randomly within the amorphous phase. The lamellae are linked to each other by tie

molecules. Yet, this two-phase description, fully crystalline and fully amorphous phases, has proved to be over simplistic, since an intermediate all-*trans* non-crystalline phase was also observed (Barron [2008]).

For sterilization purposes, the UHMWPE components are irradiated. During irradiation the breakage of polymers chains is highly intensified and free radicals are created. These free radicals combine preferentially with the available Oxygen, which diffuses through the amorphous region, provoking scission of the long chains within the UHMWPE. This phenomenon increases the amorphous regions and creates cracks, contributing to a premature failure of UHMWPE components (Goldman [1998]). To reduce this problem, actually the UHMWPE components are packed in a low oxygen atmosphere and irradiated (Greenwald [2005]).

The natural aging of UHMWPE leads to oxidation and chain scission provoking embrittlement and degradation of its mechanical properties. The chain scission process allows crystal growth to occur, increasing the degree of crystallinity of aged UHMWPE (Fouad [2010]).

In spite of the increase in the crystallinity in the aged UHMWPE, a reduction of the elastic modulus, yield and fracture stresses and creep resistance is verified. The chain scission that occurs during aging of UHMWPE leads to shorter molecules with higher mobility. Thus they can pack more efficiently into the lamellae leading to an increase in overall crystallinity and density (Kurtz [1999b]). The chain scission also affects the tie molecules by decreasing the effectiveness in supporting load leading to the breakage of the polymer long chains, reducing the molecular weight, increasing the brittleness, and weakening the properties of aged UHMWPE (Fouad [2010]).

At room temperature or body temperature, the oxidation of UHMWPE takes years to reach an appreciable level that may result in n decay of mechanical performance. Thermal aging techniques were developed to accelerate the rate of oxidation of irradiated UHMWPE. The material behavior after accelerated aging is assumed comparable to naturally aged ones. The standard method [ASTM F2003 - 02(2008)] permits the evaluation of oxidative stability in a relatively short period of time, i.e. weeks.

However, until now, after intensive work based on the accelerated aging protocols for irradiated UHMWPE in the last decade, there is not a consensus on the most effective technique to simulate shelf and *in vivo* aging. This allegedly ideal accelerated aging procedure should reproduce the chemical changes in UHMWPE. Concomitantly the depth profiles of these changes should be also reproduced (Rocha [2009]). In this sense, no accelerated aging tests, capable to replicate shelf and *in vivo* ageing of UHMWPE and HXLPE, have been convincingly assessed (Wille [2006]).

The post-irradiated oxidation process in UHMWPE is basically the same under temperatures ranging 20-80ºC (Costa [2008]). These conclusions validate the thermo-oxidation protocols for accelerated aging to reproduce in air oxidation of irradiated UHMWPE.

Numerous protocols have been proposed for accelerated aging of UHMWPE (Kurtz [1999a]). Yet, the current standard protocols [ASTM F2003 - 02(2008)] for accelerated aging of UHMWPE in air are based on two distinct techniques; Method A: aging in a air furnace at 80°C at 1 atm during 23 days (Sun [1994]); Method B: 60° and 70°C under a pressure of 5 atm of pure oxygen during 14 days (Sanford [1995]).

The oxidation depth is different for both protocols (Edidin [2002]). In the method B, the surface and the subsurface are both oxidized conversely in the method A only the surface of the specimens is degraded.

Using the method B, one week of accelerated test corresponds to 5 - 10 years of shelf aging (Sanford [1995]). Accelerated aging under method B, i.e. 14 days, is equivalent to approximately 8 years of shelf aging (Sun [1996]).

However, for comparison purposes, it is important to realize that the level of oxidative degradation produced by an accelerated aging technique is influenced by several factors such as moisture, temperature and heating rate among others (Lu [2002], Kurtz [1999b]).

A more complex reality arises during *in vivo* oxidation. When the UHMWPE components are implanted in the human body, they stay permanently surrounded by the body fluids which contain molecular oxygen necessary for *in vivo* oxidation. Actually, dissolved molecular oxygen is considered the main driving force that fuels the oxidation

reactions in implanted UHMWPE components. Since these components are gamma irradiated, they contain unstablized free radicals that are responsible to initiate *in vivo* oxidation of UHMWPE (Kurtz [2009a]).

Realistic accelerated aqueous aging protocols for gamma sterilized UHMWPE are complicated. Elevated temperatures accelerate the degradation process but lead to clinically non-relevant oxidation products for long aging times at 60°C, and for all aging times at 70°C (Mazzucco [2006]). It seems that at 50ºC in an aqueous environment is an aging protocol that avoids the non-physiological kinetics and allows accelerated oxidation. Although, under such conditions, more than a year of *in vitro* aqueous aging will be necessary to reproduce the oxidation levels observed in long-term implanted UHMWPE retrievals (Mazzucco [2006], Kurtz [2009d]).

The inherent complexity of *in vivo* oxidation process was made evident from a recently *in vitro* study (Oral [2012]). It was found that under *in vitro* accelerated aging conditions a synovial fluid lipid with unsaturated bonds (squalene), accelerated oxidation in irradiated and melted UHMWPE. Previously it was demonstrated that UHMWPE absorbs lipids from the synovial fluid *in vivo* including squalene, which is an unsaturated precursor in cholesterol synthesis among others (Costa [2001]). As pointed by Oral et al. [2012], there are other components in the synovial fluid, which may further affect the oxidation rate of UHMWPE.

The recent analysis of a second-generation HXLPE, used as liner in THA, has shown that after 5 years the wear rate remains low (Callary [2013]). This is considered a good indicator for the long-term performance of this material. Yet, the use of HXLPE in TKA remains at least inconclusive (Long [2012], Sakellariou, [2013]).

Meanwhile, two unexpected failures of THA with annealed HXLPE liners 7-8 years after being implanted were reported (Hara [2013]). Although the HXLPE achieved low wear rates, the oxidation may caused the fracture of the rim–dome junction in both liners.

Another recent study revealed that vitamin E–stabilized HXLPE performed well *in vitro* (Haider [2012]). After accelerated aging, in pure oxygen at 5 atm and 70ºC [ASTM F2003 - 02(2008)], the mechanical strength and toughness were retained along with a

low wear rate. Clearly, aging in aqueous environment would be necessary to confirm this performance for long term *in vivo*.

In a review study conducted by Kurtz et al [2011], it was concluded that the HXLPE liners in THA have a much lower risk of osteolysis than the conventional UHMWPE. Conversely, reported studies about the clinical performance of HXLPE in TKA, at that time, were too scarce to draw any conclusions. Afterwards, the effect of the use of alternative bearings for TKA (CoCr-HXLPE) was reported by Inacio et al [2013]. It was proved that in short-term they posed the same risk of all-cause, aseptic, and septic revision than traditional bearings. The benefits in long-term remain to be seen (Inacio [2013]).

7. Characterization of irradiated UHMWPE and UHMWPE-MWCNTs nanocomposites

Crosslinking of the polymer chain is the first step towards achievement of improved wear resistance. Three methods are being used for crosslinking the polymers: radiation-induced crosslinking, chemical-induced crosslinking, and silane compound-induced crosslinking. Among these three methods, the radiation induced crosslinking has dominated in medical applications as the other crosslinking techniques influenced the biological reaction in the body, Aquino [2012]. Gamma irradiation of UHMWPE induced several changes in its structure. The properties of irradiated UHMWPE were influenced by the irradiation dose and its environment. Premnath et al. [1999] reported that the crosslinking of UHMWPE dominated when irradiation was done in absence of air, whereas chain scission of polymer was observed to dominate in air environment. It is a known fact that the crosslinking enhances the wear resistance and the toughness of UHMWPE, while the chain scission reduces the mechanical properties by breaking the back bone of the polymer chain. However, it is a known fact that the mechanical properties of UHMWPE are relatively degraded due to the oxidation of the polyethylene by the irradiation generated free radicals. Oxidation of the polymer was found to be one of the major problems encountered as a consequence of crosslinking. In order to overcome the same, the irradiation process was combined with thermal treatment as a technology to improve the wear and oxidation resistance of UHMWPE, Muratoglu et al.

[1999], McKellop et al. [1999], and Muratoglu et al. [2001]. The subsequent discussion is focussed on the influence of irradiation on the mechanical and wear characteristics of UHMWPE and UHMWPE/MWCNTs composites.

7.1 Irradiation of UHMWPE

The prime purpose of irradiation is to enhance the wear resistance of UHMWPE, but nonetheless it has deteriorating effects on the mechanical properties due to free redical induced oxidation. A report of few studies which demonstrated the influence of irradiation on the wear resistance of UHMWPE is discussed herein. Oonishi et al. [1997] studied the wear resistance of irradiated UHMWPE against an alumina ball using a sphere-on-plate reciprocating testing machine. It was reported that the wear resistance of UHMWPE was increased with irradiation dose in comparison to that of unirradiated specimen. However, the coefficient of friction of the test sample was not influenced by the irradiation, but the hardness of the samples was increased. Lee et al. [2009] performed scratch and wear tests on a prosthetic femoral head against crosslinked UHMWPE sockets using a 8- station hip wear simulator for 2 million cycles. The authors reported that the abrasive wear of UHMWPE was reduced by 97 % against Zirconia toughened alumina compared to CoCr. In case of oxide coated Zirconium-Niobium femoral head, the abrasive wear resistance of UHMWPE was increased by 161 % compared to CoCr. Bashyal et al. [2011] opined that the benefits of improved wear resistance and low rate of osteolysis of highly crosslinked polyethylene outweighed the concerns of ageing degradation of the properties. Sugano et al. [2004] studied the wear rate of 1000 kGy irradiated UHMWPE acetabular cup retrieved after 25 years of its usage under *in vivo* condition. It was reported that the wear rate of retrieved cup was found to be 0.04 mm/year whereas the conventional cup under *in vitro* condition had the wear rate of 0.06 mm/year. Muratoglu et al. [2002] irradiated UHMWPE using 2 MeV electron beam at 140 ^{o}C to obtain the limited penetration effect of irradiation. The wear studies on irradiated sample using a 12-station hip simulator showed that there was no significant mass loss after a million cycles whereas the conventional material showed the wear rate of 27 mg/million cycles. It was concluded that the high crosslink density near the articulating surface of the sample improved the wear resistance of the acetabular liner significantly.

The effects of irradiation on the mechanical properties of UHMWPE from selected literature are summarized in Table 3.

Table 3. Influence of irradiation on mechanical properties of UHMWPE

Dosage	Young's modulus	Fracture stress	Yield stress	% Strain at fracture	Researcher
200 kGy in air	-	Reduced from 46 to 29 MPa, i.e. 37%	Reduced from 22 to 19 MPa, i.e. 13.6 %	-	Muratoglu et al. [1999]
100 kGy after 6 years of *in vivo* ageing	-	-	Reduced 30.3 to 24.7 MPa, i.e. 8.5 %	Reduced from 4.27 to 0.12, i.e. 97 %	Puertolas et al. [2001]
500 kGy irradiation in air	-	Reduced from 37 to 33 MPa, i.e.10.8 %	-	Reduced from 50 to 23, i.e. 54 %	Kang et al. [2001]
250 kGy irradiation in air	-	Reduced from 53.4 to 33 MPa i.e. 58.2 %	-	Reduced from 711 to 32 i.e. 95 %	Suarez et al. [2003]
25 kGy irradiation at 100 ^{0}C	Increased from 0.81 to 0.87 GPa i.e. 8 %	Increased from 47.7 to 53.3 MPa i.e. 12 %		Reduced from 3.67 to 3.10 i.e. 15 %	Nakamura et al. [1998]
Gamma irradiation 25 kGy and accelarated aged for 36 hrs	-	Reduced from 37 to 14.1 MPa i.e. 61.8 %	Reduced from 18.6 to 16.7 MPa i.e. 10.2 %	Reduced from 5.31 to 0.92 i.e. 82 %	Medel et al. [2004]

It is observed from Table 3 that the irradiation led to the reduction of mechanical properties, which depends on the dose of irradiation and the ageing period. The percentage strain at fracture of UHMWPE, as observed in the Table 3, was reduced considerably after irradiation, i.e the irradiation made the polymer more brittle and thus it is more easily prone to fracture. It is also noted from the above table that the fracture stress and yield stress were also reduced in all the reported studies, except Nakamura et al. [1998]. In a majority of literature reviewed by Lewis [2001], it was pointed out that the irradiation led to an improvement of the strength of the material immediately after irradiation, but it was reduced gradually due to oxidation of the material. Post irradiation thermal treatments are used to minimize the loss of the mechanical properties by mobilizing the trapped free radicals in UHMWPE, but it leads to the reduction of fatigue and fracture toughness of the polymer, Muratoglu et al. [2001]. The beneficial effects of radiation crosslinking in terms of increased wear resistance can be sufficiently extracted if the problem of oxidation is counteracted. In order to overcome the same, α-tocopherol (α_T, Vitamin E) is being added to UHMWPE. Nonetheless, addition of α_T has led to the reduction of the crosslinking process. Recent studies performed by Morlanes et al. [2012] and Sreekanth et al. [2012, 2013c] have shown that MWCNTs exhibited good antioxidant properties and thus it can be used to reduce the oxidative degradation of mechanical properties of UHMWPE. It is also simultaneously improved the wear resistance of UHMWPE.

7.2 Irradiated UHMWPE/MWCNTs composites

A study on irradiated UHMWPE/MWCNTs composite has been a topic of recent interest. The performance of UHMWPE/MWCNTs composites after irradiation depends on the interaction of MWCNTs with irradiation source and the surrounding UHMWPE matrix. According to Dresselhaus et al. [2001], MWCNTs have a wide variety of defects, resulting from the manufacturing stages, processing and the irradiation. Different defects such as point defects (vacancy and interstitial defects), strains, pentagon-heptagon pairs, pentagon-octagon-pentagon pairs etc were observed so far in the MWCNTs, which interact with the surrounding matrix influencing the final properties of the composites. It was reported by Watts et al. [2003] that the irradiated MWCNTs detain a significant number of defects as well as significant structural modifications. These defective sites of MWCNTs were more reactive than the perfect

nanotubes due to their high electron affinities, Zhou et al. [2003] and Chakrapani et al. [2003], and may act as radical traps in chemical processes and an antioxidant. Although several studies were reported with vitamin E as an antioxidant for UHMWPE, not many studies were reported to explore the potentialities of MWCNTs as an antioxidant during the irradiation process. The recent studies conducted by Morlanes et al. [2012] and Sreekanth et al. [2013c] are in this direction and will be discussed below in detail.

Morlanes et al. [2012] incorporated chemically unmodified MWCNTs up to 3 wt. % into UHMWPE and irradiated the composites with 90 kGy irradiation dose. The authors performed accelerated ageing in air for 36 hours and then studied the oxidation index and radicals concentration. It was reported that the number of radicals generated in the composite by gamma irradiation process was decreased when MWCNTs concentration increases. The electron spin resonance (ESR) studies reveales that the presence of allyl radicals was seriously affected by the introduction of MWCNTs. Though the allyl radicals were also observed in the irradiated MWCNTs composites, their intensity was lower than that of pure UHMWPE. It was found that the presence of MWCNTs not only reduced the amount of free radicals but also influenced the type of radical species in UHMWPE. At lower concentration of MWCNTs, the allyl radicals were found to be evident, whereas at higher MWCNTs concentration, vinyl and polyenyl radicals were observed to be prominent. Fourier transform infrared spectroscopy measurements on the accelerated aged samples pointed that the oxidative stability of the composite was found to be increased with MWCNTs concentration. The oxidation index of UHMWPE/MWCNTs composites was reported to be unchanged during the period of accelarated ageing. This study also showed that the presence of MWCNTs did not affect the crosslink density of UHMWPE unlike vitamin E, where the crosslink density was not found to vary considerably compared to pure UHMWPE subjected to the same irradiation dose. It was concluded that MWCNTs acted as radical scavengers and are more efficient in the reduction of persistant long term radicals thus they could be a good alternative to other conventional antioxidants such as vitamin E currently used in UHMWPE.

Sreekanth et al. [2013c] reported a more detailed study on the effect of MWCNTs in restricting the degradation of mechanical properties by considering the effect of ageing at different time periods. UHMWPE was reinforced by MWCNTs up to 2 wt. % and then subjected to gamma irradiation doses of 25, 50, 75 and 100 kGy. The irradiated samples were shelf aged at different period times, such as 10, 60 and 120 days after

irradiation, and its mechanical properties, and relative radical intensity were studied in detail.

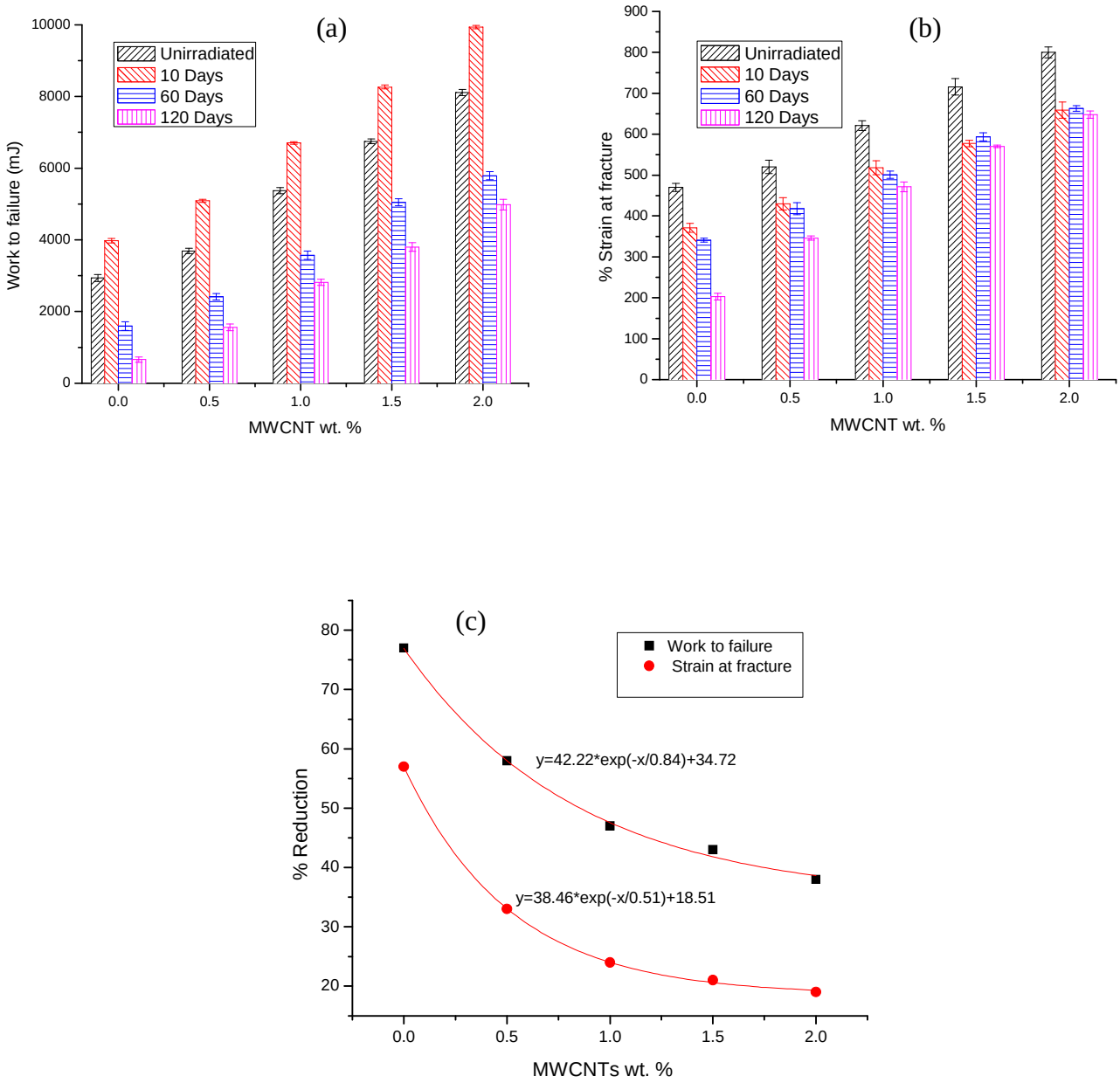

Figure 8. Influence of ageing on (a) work to failure and (b) strain at fracture of nanocomposites (c) percentage reduction of properties of nanocomposites after 120 days of 100 kGy irradiation dose compared with respective unirradiated sample.

The mechanical properties of the UHMWPE and its composites were studied at different irradiation doses and ageing periods. The influence of ageing on work to

failure at 100 kGy irradiated test samples against the concentration of MWCNTs is shown in Fig. 8a. The work to failure of the polymer and nanocomposites is shown at different stages: before irradiation, within 10 days, 60 and 120 days after 100 kGy irradiation. It was observed that the work to failure of pure UHMWPE and 2.0 wt. % MWCNTs reinforced UHMWPE was increased by 40 and 22%, respectively immediately after the irradiation process, but it was found to be reduced after 60 and 120 days of irradiation. The reduction of work to failure of the 100 kGy irradiated pure UHMWPE and 2 wt. % UHMWPE nanocomposites after 60 days of irradiation was found to be 45.7 and 28.5%, respectively in comparison with unirradiated virgin powder and a reduction after 120 days of irradiation was found to be 77.5 and 38%. The reason for the enhancement of work to failure immediately after the irradiation process and the reduction after 60 and 120 days of irradiation is explained by the mechanism of crosslinking and oxidation of the free radicals formed during the irradiation process. The interaction of gamma radiation with the polymer produced primary radicals, which led to chain scission and crosslinking. Both the processes occurred simultaneously during the irradiation of polymer, and the chain scission led to the reduction of mechanical properties, while the crosslinking of polymer increased its work to failure, failure stress and yield stress. The enhancement of mechanical properties immediately after the irradiation process was also ascertained to the increased crystallinity of the polymer due to the crosslinks formed in the amorphous region through the introduction of radicals induced by irradiation. Thus, it led to an enhancement of work to failure immediately after irradiation. The reduction of properties after 60 and 120 days of irradiation was reasoned by the fact that the radicals generated in the crystalline phase of the polymer did not have sufficient mobility, leading to a slower diffusion into the amorphous regions leading to the oxidation of the polymer enabling the further degradation of the material.

On the other hand, the strain at fracture of the test samples was reduced after irradiation and ageing period, as it is shown in Fig. 8b. It was reported that the effect of ageing on the reduction of strain at fracture can be negligible beyond 1 wt% of MWCNTs. The percentage reduction of work to failure and strain at fracture of the 100 kGy irradiated nanocomposites after 120 days of shelf ageing against their respective unirradiated sample is shown in Figure 8c. The work to failure and strain at fracture of UHMWPE irradiated at 100kGy were reduced by 77 and 57%, respectively compared to that of unirradiated UHMWPE, whereas the respective reduction was limited to 38 and 19%

for the UHMWPE / 2 wt. % MWCNTs sample irradiated at 100 kGy. It was also reported that the reduction of work to failure and strain at fracture due to degradation of the polymer was decreased exponentially with an increase of the MWCNTs concentration.

The reason for the reduction of property degradation of the UHMWPE due to MWCNTs was ascertained to the formation of defects on the surface due to irradiation, resulting in pinning of MWCNTs to the polymer through the formation of chemical bonds leading to compensation of the loss of mechanical properties at higher irradiation doses. The formation of defects was confirmed through both Raman spectroscopy and transmission electron microscope (TEM). Raman studies showed that the defects generated on MWCNTs increased with irradiation dose. Several defects like variation in internal and external diameter of carbon nanotubes, coil defects, zig-zag defects and other surface defects were also identified under TEM. Electron spin resonance studies revealed that the relative radical intensity was reduced with an increase of MWCNTs concentration. In case of pure UHMWPE after 120 days of 100 kGy irradiation, the relative radical concentration was calculated to be 137, and it was reduced to 79 (42.3 % reduction) for 2 wt% nanocomposite. The authors concluded that the presence of MWCNTs has effectively restricted the concentration of radicals in the nanocomposites compared to pure UHMWPE. It was also inferred that MWCNTs helped to restrict the deteriorating effects of oxidation and thus increased the longevity of the irradiated UHMWPE.

Based on the above studies, it can be inferred that MWCNTs showed antioxidant characteristics. Unlike the conventional antioxidant Vitamin E, MWCNTs do not hinder the process of crosslinking but rather promote it. However, no studies so far have been reported, regarding to the combined influence of irradiation and MWCNTs reinforcement on the wear behaviour of UHMWPE. The exploration of MWCNTs in biomedical application is underway. Since a large part of the human body consists of carbon, it is generally thought to be a very biocompatible material and it has a significant potential, Drexler [1992]. In any case, the studies on MWCNTs aimed at biomedical applications are still active area of research.

8. Viscoelastic behavior and dynamic characterization using DMA

Most polymer systems exhibit nonlinear viscoelastic/viscoplastic behavior, which can be a very demanding experience in terms of its full characterization (Waldman [1994], Guedes [1998]). Creep occurs when the UHMWPE components are subjected to tensile or compressive stresses. The creep strain can be recovered partially, depending on the stress level, the duration of its application and the constraining environment (Wilding [1978]). UHMWPE components in orthopedic devices are machined to tight tolerances. Therefore creep and strain accumulation, on the long-term, can hamper the maintenance of these tight tolerances. Excess of creep, in an acetabular liner or tibial tray for example, can provoke dislocations or shorten the leg. The bedding-in period that occurs in the first 2 years is attributed primarily to creep of the UHMWPE (Spiegelberg [2009]). Further, and according to Pezzotti at al [2011], in several UHMWPE acetabular cups it was observed that the permanent deformation due to viscoplastic deformation and wear were the two main degradation processes responsible for their failure. Thus, viscoelastic/viscoplastic behavior of UHMWPE must be restrained as much as possible.

8.1 Creep testing and modeling

Although, for computational wear analyses purposes, the UHMWPE viscoelastic/viscoplastic deformations may play a very important role in the wear phenomenon, this type of behavior has been scarcely considered in the literature (Quinci [2014]). Moreover the crack initiation from a notch in UHMWPE is a complex phenomenon that is governed by the viscoelastic fracture theory (Sirimamilla [2012]). In brief, the importance of considering the viscoelatic/viscoplastic behavior of UHMWPE for medical application has been further emphasized by recent research.

The discussion that follows will be restricted to the field of infinitesimal strain theory for viscoelastic and viscoplastic solids. For the finite strain theory applied to UHMWPE the readers are referred to the work developed by Bergström et al [2002], [2003] and [2004].

The research work developed by Green and Rivlin [1957], [1960], Green, Rivlin and Spencer [1959], Noll [1958] and Pipkin [1964], based on functional analysis, resulted

into the representation of constitutive equations for creep, or relaxation, in integral series. For the uniaxial case we have

$$\varepsilon(t) = \int_0^t \varphi_1(t-\xi_1)\frac{d\sigma(\xi_1)}{d\xi_1}d\xi_1 + \int_0^t\int_0^t \varphi_2(t-\xi_1, t-\xi_2)\frac{d\sigma(\xi_1)}{d\xi_1}\frac{d\sigma(\xi_2)}{d\xi_2}d\xi_1 d\xi_2 + \int_0^t\int_0^t\int_0^t \varphi_3(t-\xi_1, t-\xi_2, t-\xi_3)\frac{d\sigma(\xi_1)}{d\xi_1}\frac{d\sigma(\xi_2)}{d\xi_2}\frac{d\sigma(\xi_3)}{d\xi_3}d\xi_1 d\xi_2 d\xi_3 + \cdots \quad (1)$$

The complete determination of the kernels $\varphi_i(...)$ is very involving and time consuming (Findley, [1989]).

A simpler and effective approach was given by Schapery [1969].The theory has proven to describe reasonably well the non-linear viscoelastic behaviour for several polymers [Lai [1996]). The constitutive equation in terms of strain is restricted to small strains by the underlying thermodynamic theory. For the unidirectional case is given as

$$\varepsilon(t) = g_0 S_0 \sigma(t) + g_1 \int_{0^-}^t \Delta S\left(\psi - \psi'\right)\frac{d\left(g_2\sigma(\tau)\right)}{d\tau}d\tau + \left\{\varepsilon(t)\right\}_{vp} \quad (2)$$

where S_0 is the elastic compliance, $\Delta S(t)$ is the linear transient creep compliance , ψ e ψ' the reduced time,

$$\psi = \int_{0^-}^t \frac{d\tau'}{a_\sigma} \text{ and } \psi' = \int_{0^-}^\tau \frac{d\tau'}{a_\sigma} \quad (3)$$

and $g_0(\sigma)$, $g_1(\sigma)$, $g_2(\sigma)$ and $a_\sigma(\sigma)$ are the stress dependent nonlinear functions.

This model was modified by including a viscoplastic term with good results for polymer based composites by Tuttle et al [1995] and Guedes et al [1998], based on the work done by Zapas and Crissman [1984] on the creep-recovery behavior of UHMWPE. The viscoplastic strain for the unixial case is given by

$$\left\{\varepsilon(t)\right\}_{vp} = \phi\left\{\int_{0^-}^t g_3\left[\sigma(\psi)\right]d\psi\right\} \quad (4)$$

where $\phi\{\ \}$ is a stress dependent functional.

Zapas e Crissman [1984] verified that the viscoplastic behavior of UHMWPE was well represented by the following functional

$$\phi\left\{\int_{0^-}^{t} g_3\left[\sigma(\psi)\right]d\psi\right\}=\left\{\int_{0^-}^{t} g_3\left[\sigma(\psi)\right]d\psi\right\}^n \tag{5}$$

where the exponent *n* is a material property independent of stress level but temperature dependent. The function $g_3(\sigma)$ was assumed to be stress dependent, in the following form

$$g_3(\sigma)=\mathrm{C}\cdot\sigma^N \tag{6}$$

where *C* and *N* are material parameters, stress independent, but dependent on the temperature level.

The Prony series are convenient to represent the transient creep compliance as follows,

$$\Delta S(t)=\sum_{i=1}^{n} S_i\left(1-e^{-\lambda_i t}\right) \tag{7}$$

The creep and recovery behaviour of an UHMWPE was studied in the region of small uniaxial deformations by Zapas and Crissman [1984]. These results are used to illustrate the capability of the Schapery model to represent the viscoelastic/viscoplastic behaviour of UHMWPE. Creep and recovery experiments were carried out on specimens under creep stresses in the range 1-8 MPa. In Figure 9 are plotted the creep compliances obtained, showing to be stress dependent above 1 MPa. Using the appropriate values for the model parameters, the strain under creep and creep-recovery loading conditions were very well captured as shown in Figure 10.

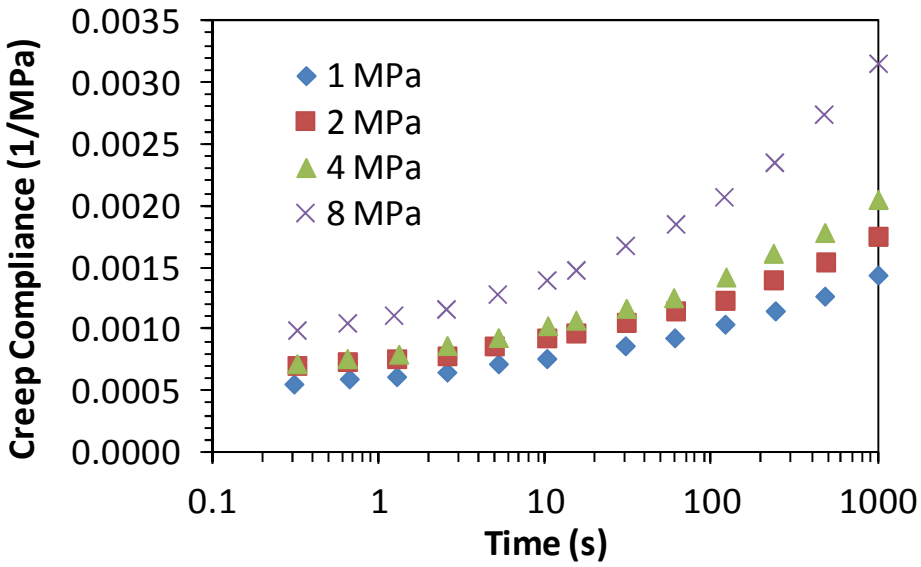

Figure 9: Experimental creep compliance for UHMWPE for different stress levels.

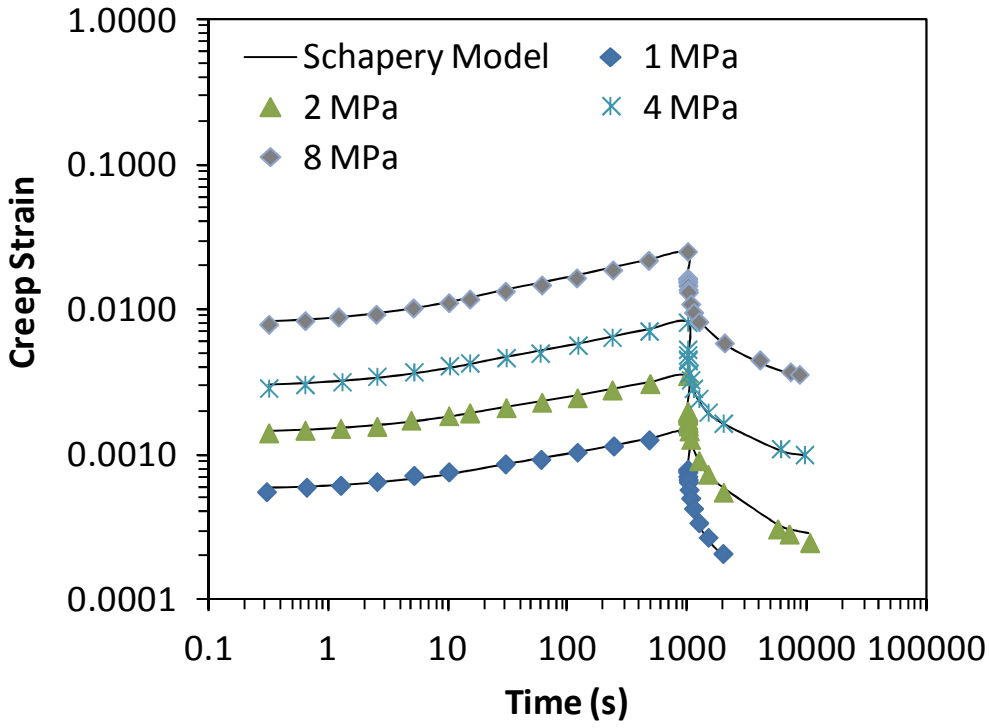

Figure 10: Experimental and theoretical prediction for UHMWPE strain under creep and creep-recovery after 1000 s loading conditions for different stress levels.

The viscoplastic strain accumulated under creep loading conditions, after 1000 s, depends on the stress level as shown in Figure 11. For the highest creep stress level, 8 MPa, the viscoplastic strain corresponds to 14% of total strain after 1000 s.

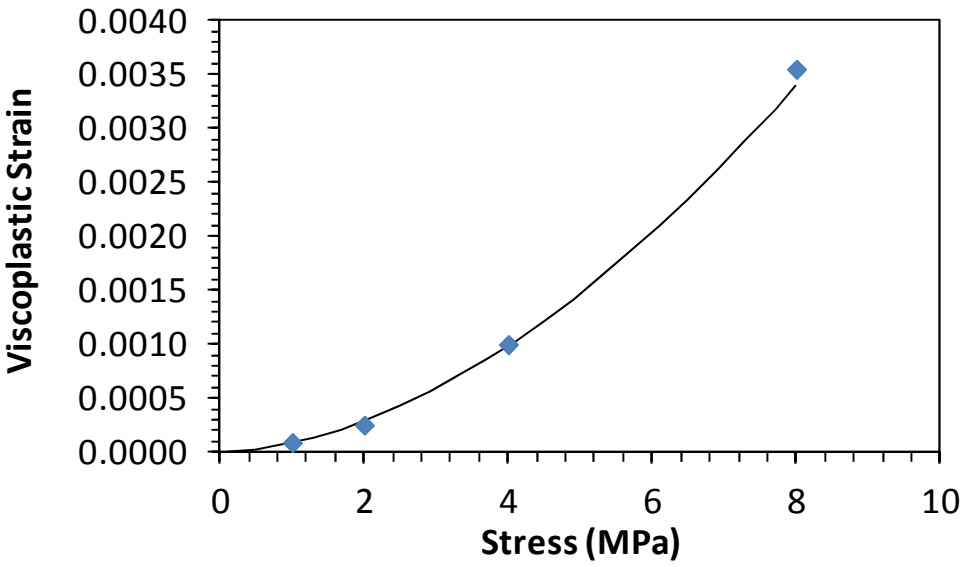

Figure 11 :Viscoplastic strain for UHMWPE after 1000 s.

It should be pointed that most contact stresses observed in THA are below 8 MPa (Teoh [2002]). This stress level is considered a critical value related to UHMWPE plastic deformation (Teoh [2002]). Thus, from the previous results, it can be concluded that even below a stress level of 8 MPa it can be expected significant viscoplastic strain accumulation for the UHMWPE.

For creep stress levels higher than 8 MPa, the mechanical behavior of UHMWPE starts to manifest high strain levels, as shown in Figure 12. The plotted data was obtained from the experiments conducted by Bhateja and Andrews [1983].

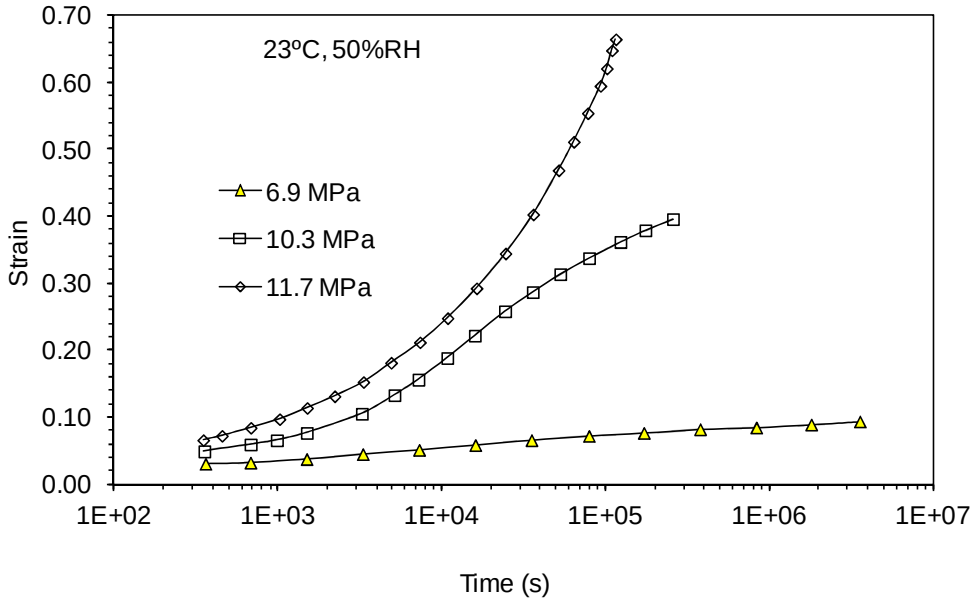

Figure 12: Experimental creep strain for UHMWPE for different stress levels. From (Bhateja and Andrews [1983]).

The crosslinking, irradiation, increases the creep resistance of UHMWPE. This was observed by Bhateja and Andrews [1983], as shown in Figure 13.

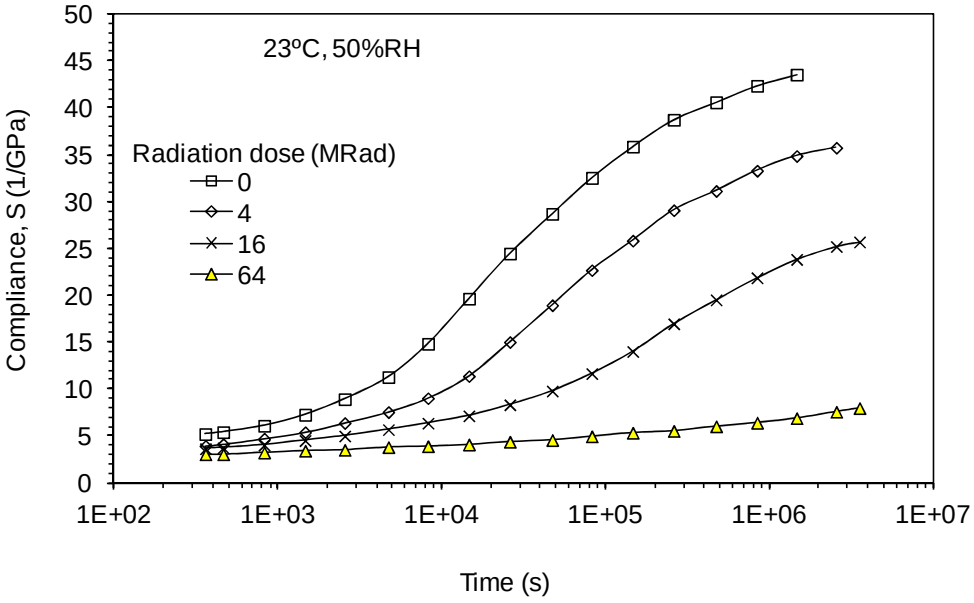

Figure 13: The effect of irradiation on creep compliance for UHMWPE for different radiation doses. From (Bhateja and Andrews [1983]).

As shown by Lee et al. [2005] the crosslinking and the crystal morphology changes were the main microstructural modifications that occurred after irradiation, which alter the mechanical properties of UHMWPE. In general, the static mechanical properties and the creep resistance are enhanced after irradiation.

Deng et al. [1998] studied the short- and long-term creep behaviors of UHMWPE. The short-term creep experiments under 1 MPa lasted less than 2 hours at a temperature range of 37-62°C. The long-term creep behavior of UHMWPE systems at 1 MPa and 37°C was predicted using time-temperature superposition principle (TTSP), based on short-term creep data. The TTSP will be briefly explained latter. Whereupon, three empirical formulas were suggested to represent the creep compliance. Those equations are here referred by Equation A, B and C,

Equation A: $S(t) = c_A (\log t)^{b_A}$ (8)

Equation B: $S(t) = c_B t^{b_B}$ (9)

Equation C: $S(t) = c_C + b_C \log t$ (10)

For each equation, the number of model parameters is always three.

The prediction obtained from the TTSP for UHMWPE was compared against extrapolation of analytical formulas that were fitted to the short-term creep data under a tensile load at 37°C and 1 MPa. This comparison is given in Figure 14 where it can be observed that Equation C yielded a good agreement with TTSP prediction. However when compared to actual long-term creep experiments for 110 days, the Equation A was found to predict quite well the creep compliance of UHMWPE, as shown in Figure 15.

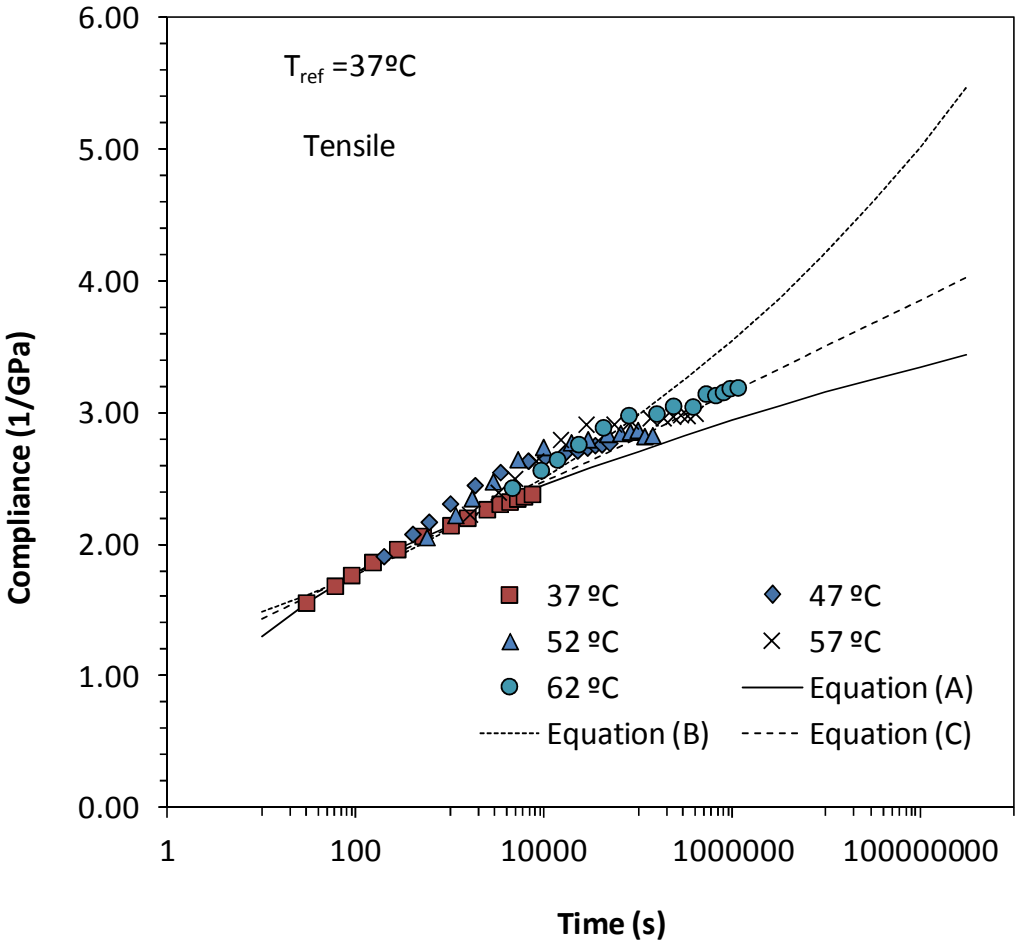

Figure 14: Comparison of the prediction by time–temperature superposition for UHMWPE with extrapolation of the curve-fit the short-term creep data under a tensile load at 37°C and 1 MPa. From (Deng [1998]).

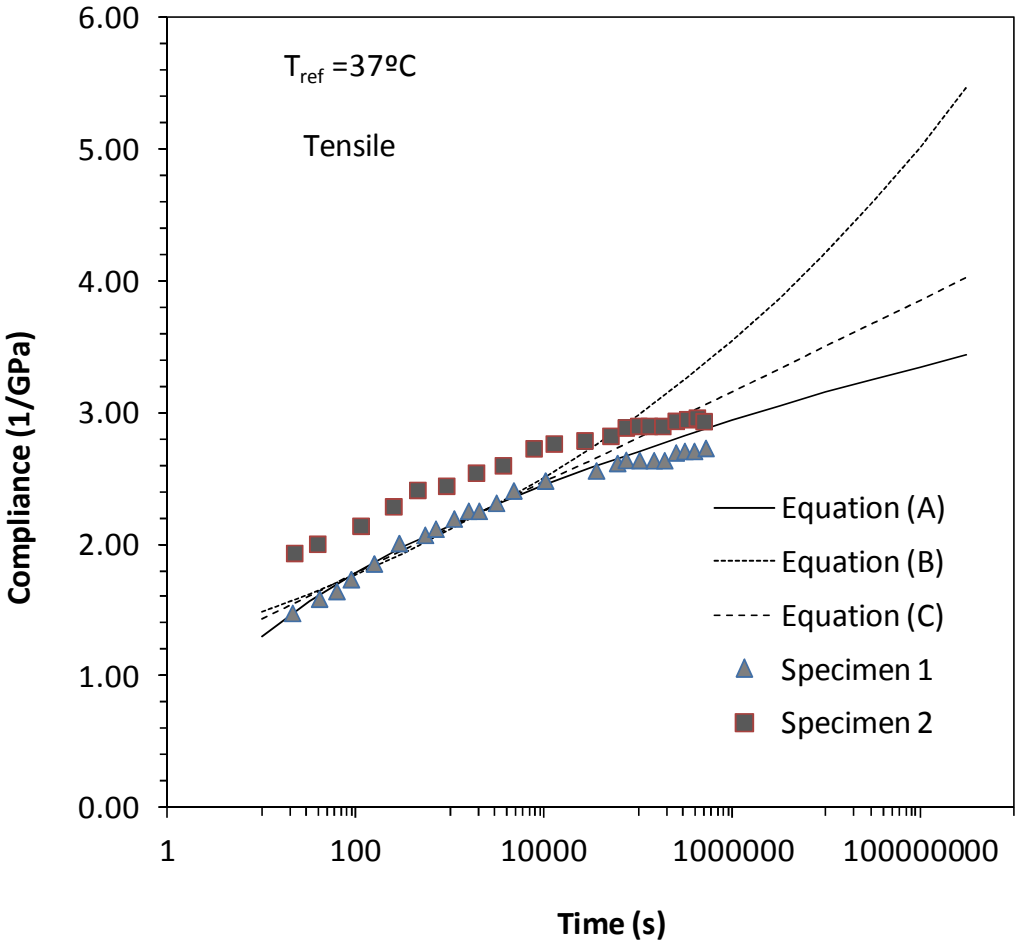

Figure 15: Comparison of actual creep (specimens 1 & 2) with the prediction by time–temperature superposition for UHMWPE under a tensile load at 37°C and 1 MPa. From (Deng [1998]).

The Equation A predicts the fastest reduction rate in creep compliance development of all three equations. This feature of UHMWPE was corroborated by Lee and Pienkowski [1998] after static compressive creep tests of UHMWPE under physiologic conditions. In general terms and assuming a time span of 10 years, 90% of creep deformation occurs in the first month following the load application (Deng [1998]). The creep behaviors under tensile and compressive loading are slightly different as it was observed experimentally by Deng et al. [1998] and depicted in Figure 16.

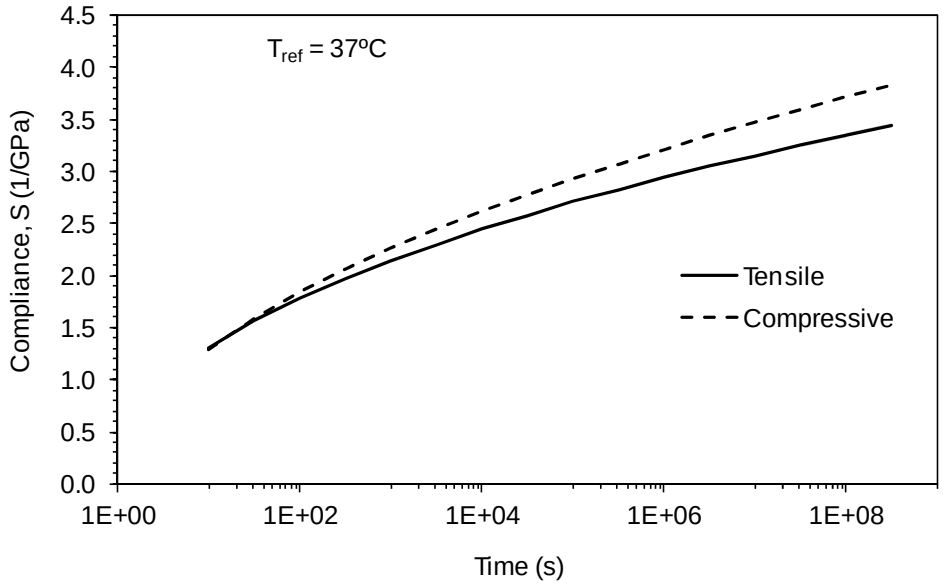

Figure 16: Comparison of creep compliance under a tensile with creep compliance under a compressive load at 37°C and 1 MPa. From (Deng [1998]).

8.2 Dynamic Mechanical and Thermal Analysis

The characterization of viscoelastic properties of polymeric materials on a DMTA (Dynamic, Mechanical and Thermal Analyser), are conducted to the determination of the complex modulus *E** as a function of angular frequency *w*. In order to characterize the viscoelastic material behavior in a very broad range of frequencies (or times), it is necessary to combine measurements at several temperatures applying the time-temperature superposition principle (TTSP). In brief, the short-term experimental data is shifted empirically to those at the reference temperature on a semi-log axis. In many cases, the material is thermorheologically simple and the shape of the distribution of relaxation or retardation times is independent of temperature. Simultaneously, the stress magnitudes at all frequencies or times display the same temperature dependence (Dealy 2009]). This procedure leads all creep compliance curves, measured at different temperature $S(T)$, collapsing into a master curve when plotted as $b_T S(T)$ versus t/a_T on a log-log scale. The shift factors a_T (horizontal) and b_T (vertical) are functions of temperature, although the b_T temperature dependence is usually weak (Delay [2009]). If the previous conditions do not hold, the material is classified as thermorheologically

complex and all the model parameters become temperature dependent (Heymans [2003]).

The fractional Maxwell model was used with great success to analyze DMTA data of UHMWPE by Guedes [2011a].The creep compliance is given by the following expression,

$$S(t) = b_T \left[S_0 + S_1 \frac{\left(\frac{t}{a_T \tau_0} \right)^{\alpha}}{\Gamma(\alpha+1)} \right] \tag{11}$$

where S_0 is the elastic compliance, S_1 and α are viscoelastic parameters, τ_0 is the reference time, i.e. 1s or 1min or 1 hour, and so on and where the reciprocal of the vertical shift and the horizontal shift are given by an Arrhenius equation as, respectively,

$$\ln\left(\frac{1}{b_T}\right) = \frac{\Delta H_b}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{12}$$

and

$$\ln(a_T) = \frac{\Delta H_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{13}$$

where *R* is the gas constant, 8.314E-3 kJ/(K mol), ΔH_b and ΔH_a are the relaxation or retardation activation energy and T_0 is the reference temperature in °K. Therefore, in this model it is assumed that the elastic modulus, which is time-independent, changes with temperature manifest a vertical shift. Furthermore, vertical shifting also affects the viscoelastic components, which are simultaneously subjected to horizontal shifting (in time). Consequently, this form does comply with the definition given by Delay and Plazek [2009] for thermorheologically simple materials.

In the frequency domain, the storage and loss compliance are given as

$$S'(w) = b_T \left[S_0 + S_1 \left(\mathrm{w}\, a_T \tau_0 \right)^{-\alpha} \cos\frac{\alpha\pi}{2} \right], \tag{14}$$

$$S''(w) = b_T S_1 \left(\mathrm{w}\, a_T \tau_0 \right)^{-\alpha} \sin\frac{\alpha\pi}{2} \tag{15}$$

The methodology to determine the elastic-viscoelastic parameters, from DMTA data, is described in detail elsewhere (Guedes [2011a]).

Experimental and modeling of dynamic viscoelastic properties of a medical grade UHMWPE (GUR 1020) was performed. The applicability of the time-temperature superposition principle (TTSP) to the dynamic viscoelastic properties was verified; both horizontal and vertical shifts were necessary to superimpose the dynamic modulus/frequency curves. The methodology proposed to determine the horizontal and vertical shifts factors for the TTSP leads to an easy and effective way to calculate these shift factors. The traditional method by curve fitting optimization can find nicely superimposed curves but has the risk of the shift parameters lacking any physical significance (Dealy [2009]). The storage and loss compliance master curves generated by curve shifting are plotted in Figure 17. The two sets of curves are simultaneously moved horizontally and vertically using the vertical and horizontal shift factors previously calculated.

Horizontal and vertical shifts comply equally well with Arrhenius equations as shown in Figures 18-19. The vertical shifts can be explained by the density and temperature product changes as assumed in the Bueche-Rouse theories of the linear viscoelaslicity of unentangled polymer melts and solutions (Dealy [2009]). Moreover, if the Delay and Plazek [2009] definition is applied, the UHMWPE may be considered thermorheologically simple, at least for the present frequency and temperature ranges tested (0.1-50 Hz and 27-62 ºC).

The ambiguities that may arise from the curve superposition, which results from curve fitting optimization, are eliminated by this methodology. Thus, this model proved to be very effective when used to compare the viscoelastic behavior of different UHMWPE materials (Guedes [2011a]), the effect of aging (Guedes [2011b]) and the effect of nano-reinforcements (Guedes [2013]).

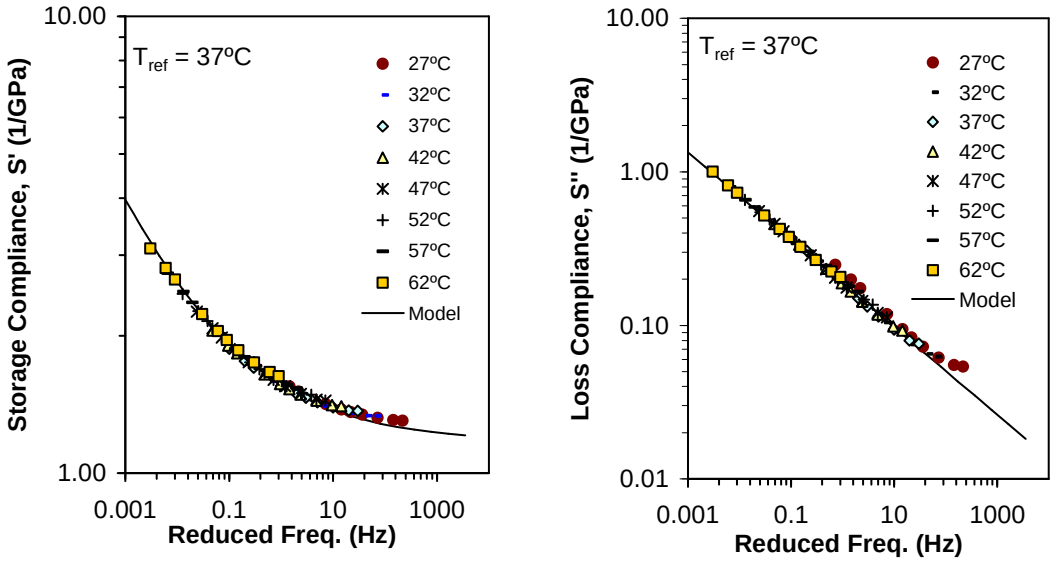

Figure 17: Storage and loss compliance shifted for the UHMWPE, at 37ºC. From (Guedes [2011a]).

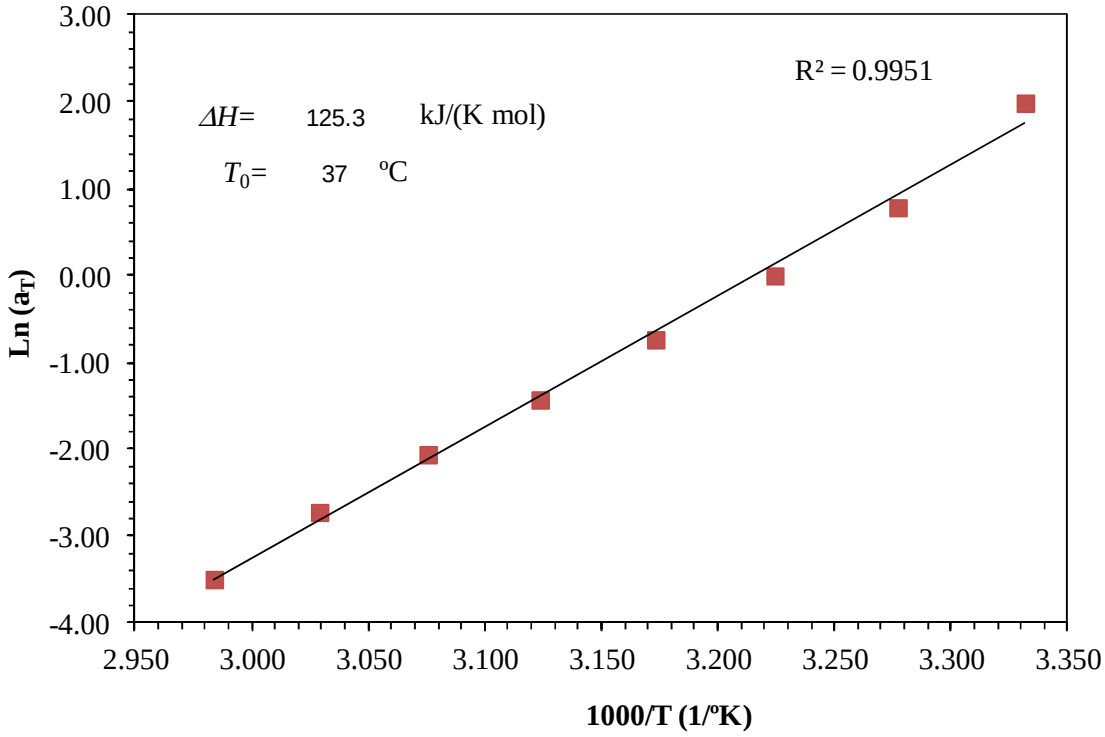

Figure 187: Horizontal shift factors for the UHMWPE at various temperatures compared against Arrhenius equation curve fitting. From (Guedes [2011a]).

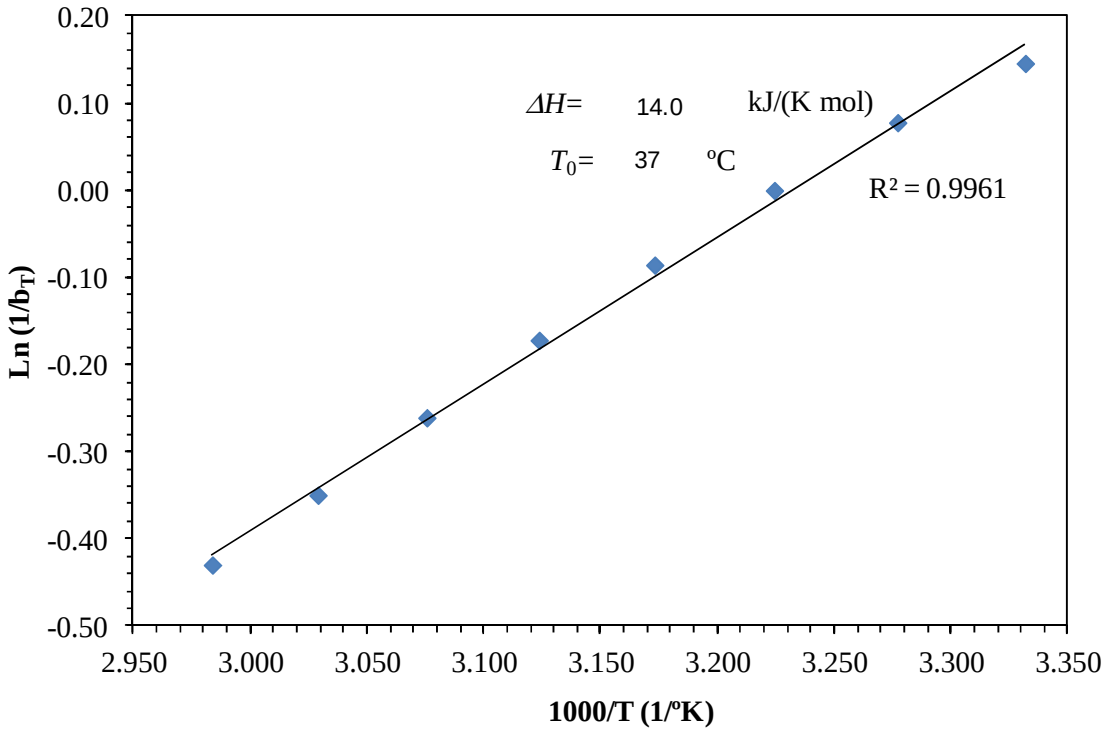

Figure 19: Vertical shift factors for the UHMWPE at various temperatures compared against Arrhenius equation curve fitting. From (Guedes [2011a]).

9. Conclusion

The main conclusion that can be drawn is related to the impressive development of UHMWPE that occurred during the last 50 years. Another relevant aspect is the complexity of UHMWPE, which complicates the lifetime analysis and mechanical behavior prediction of the UHMWPE as a bearing component in TJA and TKA. The wear of UHMWPE is dependent on a multitude of events occurring simultaneously and sequentially. Thus, the internal structure of UHMWPE (composed of amorphous and crystalline phases) is constantly being altered, provoking changes on its mechanical response and on the contact area. These interactions are still not completely understood. Wherewith, there is an oxidation process that occurs from beginning and certainly is fueled by the Oxygen dissolved in the fluids surrounding the UHMWPE. This process also degrades the mechanical properties of UHMWPE compromising its long-term survival. Thus, to tackle these problems, diverse approaches were chosen to improve the

UHMWPE mechanical behavior, including the radiation crosslinking, fiber reinforcement, and antioxidants such as Vitamin E or Vitamin C. Since these techniques induce morphological changes, they are expected to alter favorability the mechanical response of UHMWPE. Yet, the real assessments of these new solutions have been and will be done throughout *in vivo* examination of long-term follow-up of THA and TKA containing the second generation HXLPE. The future steps, for further improvement, must rely on a careful analysis of these assessments.

Finally, like any polymer, UHMWPE is a viscoelastic material, even at room temperature, i.e. it exhibits creep and stress relaxation under static and dynamic loading conditions. Within certain limits, it was shown that UHMWPE is a thermorheologically simple material (Guedes [2011a]). Remarkably, not many published papers are devoted to study the viscoelastic behavior of UHMWPE (Deng [2010]). However this is an important subject since the components are mounted with tight tolerances and UHMWPE excessive creep limits the long-term survival of TJA (Deng [1998]). Again, the importance of minimizing the UHMWPE viscoleastic behavior is very clear.

Acknowledgements

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