

## 3.4 The Crosslinked Ultra-high Molecular Weight Polyethylene: Risk and Limitation

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### Introduction

In the past three decades the majority of the implanted orthopedic prostheses included a bearing component made of ultrahigh molecular weight polyethylene (UHMWPE) articulating against a femoral metallic or ceramic ball or a metallic tibial plateau. Wear of the polyethylene bearing surfaces produces abrasion particles [1], often causing a foreign body response that may lead to bone resorption (osteolysis) and loosening of the components, and thereby limiting the life expectancy of hip prostheses. Thus, improving the wear resistance of the polyethylene can substantially extend the clinical life span of total hip prostheses.

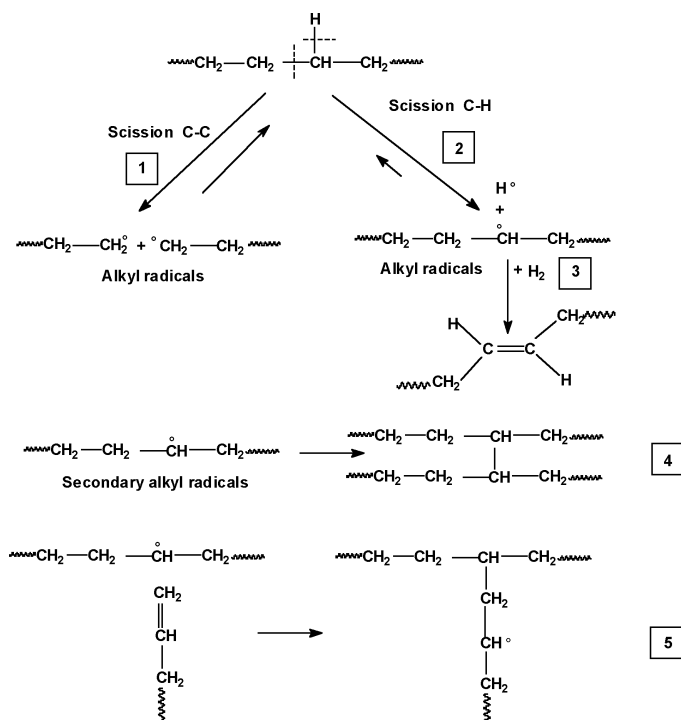
The majority of polyethylene components has been sterilized by gamma irradiation in the presence of air, with doses between 25 and 40 kGy. However, oxygen that was present in the polyethylene when it was irradiated, or that diffused into the polyethylene during shelf storage and/or in vivo, could react with the free radicals that were generated by the radiation, causing oxidative degradation that lowered the molecular mass, increased the density, stiffness and brittleness, and reduced the fracture strength and elongation to failure [2-3]. Any of these changes could adversely affect the wear resistance of the polyethylene [4-5]. In contrast, in absence of oxygen, the free radicals generated during radiation sterilization could form crosslinked polyethylene molecules [6-7], and crosslinking has been shown to markedly improve the wear resistance of polyethylene acetabular cups in laboratory wear simulators [8-11] and in clinical studies [12-16]. Consequently, orthopaedic researches were directed to the development of an UHMWPE implant that has the resistance to oxidation of the unirradiated polyethylene while possesses optimum level of crosslinking to improve its wear resistance.

### Risk

Irradiation of UHMWPE with high energy radiation (gamma or electron beam) leads to physico-chemical modifications of the polymer, which can be summarized as follows:

- a) Chemical changes. The energy of e-beam or gamma radiation is some order of magnitude higher than that of C-C and C-H bonds. Thus, irradiation causes bond scissions (scheme 1, reaction 1 and 2) and formation of alkyl macro-radicals which can survive for years after irradiation. Some of the radicals decay giving cross-linking (scheme 1, reaction 4), trans-vinylene double bonds (scheme 1, reaction 3) and elimination of vinyl double bonds with further cross-linking (scheme 1, reaction 5).
- b) Physical changes. Irradiation leads to a minimum increase in crystallinity, due to bond scissions, with a slight variation of the maximum of the melting peak, originated from a change in the lamellae thicknesses.

- c) Mechanical properties. Physical and chemical modifications of the polymeric structure induce also changes in the mechanical behaviour. Cross-linking leads to an increase in the Young modulus, while the formation of trans-vinylene double bonds give reason of a decrease in the elongation and tensile stress at failure.



**Scheme 1:**

The crosslinked process by high energy radiation.

Each producer adopt one of the following techniques: application of the maximum radiation dose compatible with the mechanical properties specified by international standards (ASTM and ISO), in order to highly cross-link the polymer and maximize the abrasion resistance or use of a lower radiation dose, enhancing the abrasion resistance, but retaining the mechanical properties. In any case, both techniques require a subsequent thermal treatment close to or above the melting temperature, in order to eliminate the residual macroradical.

The differences in the crosslinking process and in the thermal treatment give reason of the presence on the market of cross-linked polyethylenes with a wide range of chemical, physical and mechanical properties.

**Table 1:**

Comparison Among New Crosslinked Thermally-Stabilized Polyethylenes.

(The processing parameters shown in this table were compiled from various publications, and information provided by the manufacturers is subject to ongoing modification.)

Name and Manufacturer	Radiation Type and Dose	Thermal Stabilization	Final Final Sterilization	Total Crosslinking Dose and Type
Marathon™ DePuy, Inc.	γ radiation to 50 kGy at room temperature	Remelted at 155°C for 24 hours followed by annealing at 120°C for 24 h.	Gas plasma	50 kGy gamma
XLPE™ Smith & Nephew – Richards, Inc.	γ radiation to 100 kGy at room temperature	Remelted at 150°C for two hours	Ethylene oxide	100 kGy gamma
Longevity™ Zimmer, Inc.	Electron beam radiation to 100 kGy at room temperature	Remelted at 150°C for about six hours	Gas plasma	100 kGy electron beam
Durasul™ Sulzer, Inc.	Electron beam radiation to 95 kGy at 125 °C	Remelted at 150°C for about two hours	Ethylene oxide	95 kGy electron beam
Crossfire™ Stryker-Osteonics-Howmedica, Inc.	γ radiation to 75 kGy at room temperature	Annealed at about 120°C for a proprietary duration	Gamma at 25 to 35 kGy while packaged in nitrogen	100 to 110 kGy of gamma
Aeonian™ Kycocera, Inc.	γ radiation to 35 kGy at room temperature	Annealed at 110°C for ten hours	Gamma at 25 to 40 kGy while packaged in nitrogen	60 to 75 kGy of gamma

## Limitation

Abrasion of polymers is a complex process, depending on the physico-chemical properties of both the polymer and the abrading material.

In the present case, the polymer is cross-linked UHMWPE and the abrading material can be either a metallic or a ceramic surface, which have different roughness, or even a third body with various shape and hardness, such as bone or cement fragments or phosphate and ossalate crystals from the synovial fluid. The increase in the molecular mass of UHMWPE causes an increase in the resistance to abrasion with smooth abrading material (£ 10 micron). On the contrary, with rough counterfaces, the focal parameter is the toughness of the abraded material, thus the energy required for tearing material off the surface. Since the toughness of a cross-linked UHMWPE is lower than that of the untreated one, its resistance to abrasion with a material of roughness higher than 10 microns will be lower than that of virgin UHMWPE.

## Conclusion

The first clinical results of cross-linked polyethylene do not show a considerable improvement of performances. This evidence was quite predictable from the existing literature studies. A larger number of case studies is necessary in order to evaluate the objective performances of the new material in different clinical conditions.

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