A new generation of easily crosslinkable polyethylene copolymers

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Introduction: Ultra High Molecular Weight Polyethylene (UHMWPE) has been successfully used in total joint arthroplasty for more than 50 years. However, implant lifetime improvement is still an issue. The current paradigm of UHMWPE is threefold: good wear resistance and oxidative stability whilst maintaining mechanical properties [1]. Today's state-of-the-art material is highly crosslinked polyethylene (HXLPE), a high wear resistant material. However, the remaining free radicals after irradiation crosslinking can initiate *in vivo* oxidation and reduce the implant lifetime [2]. Remelting can significantly reduce the amount of remaining free radicals, but will also lower the crystallinity and therefore affect the mechanical properties [3]. Annealing does not influence the properties but also does not remove all free radicals [4]. In this paper we present a new generation of UHMWPE based on copolymerization of ethylene and a diene that forms a highly crosslinked network after only a sterilization dose of γ-radiation.

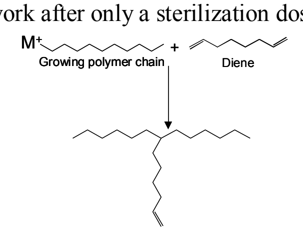

Fig. 1. Chemistry of a new generation of easily crosslinkable polyethylene copolymer.

Methods: All samples were prepared by copolymerizing ethylene and octadiene. The resulting materials were analyzed with IR and NMR to determine the amount of vinyl double bonds. Two polymers were used as linear reference materials: 1) PEs synthesized under the same conditions as the diene-copolymers but without the addition of diene comonomer and 2) MG003 (DSM). All powders were compression molded into blocks of 15 mm thickness. These blocks were γ-irradiated with 25 or 75 kGy (at Beta-Gamma-Services GmbH) and machined. Swell ratio testing was done according to ASTM F2214-02. Wear testing was performed in a Pin-on-Disc wear tester using water/serum lubrication [5].

Results: Vinyl double bonds are known to readily react with macroradicals to form Y-crosslinks upon irradiation of (UHMW)PE [6]. By introducing more pendant vinyl bonds in the PE chains, the crosslink efficiency could be increased. A lower number of radicals could be required, thus reducing the oxidative degradation *in vivo*.

To prove this concept various copolymers with increasing amounts of incorporated pendant double bonds were synthesized. Their swell ratio and wear resistance were measured after irradiating them with a sterilization dose 25 kGy of γ-radiation. The data was compared to reference samples (both linear UHMWPEs) where no diene was added to the reaction vessel (2 – 25 kGy) and to MG003 irradiated with 25 or 75 kGy (Fig. 2). The diene-copolymers show an increasing network density with increasing residual double bond content at the low radiation dose. The sample with 12 C=C per 100.000 C-atoms shows a comparable, even slightly higher, network density than the linear UHMWPE irradiated with 75 kGy. The wear factor is known to be directly related to the network density [7], which is also what was observed for this series of materials.

ESR measurements performed on the diene copolymers and linear UHMWPEs, showed that the amount of remaining (stable) free radicals is 2-3 times lower for samples irradiated with 25 kGy as compared to samples irradiated with 75 kGy. This shows that this new generation PE has indeed a reduced free radical content due to the lower irradiation dose, whilst maintaining the same degree of crosslinking. Moreover, this suggests that the irradiated diene-copolymers are more oxidatively stable than conventional HXLPE.

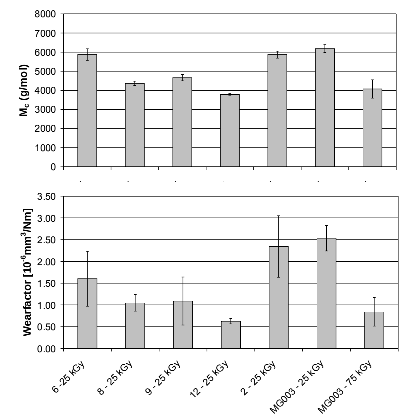

Fig. 2. MW between effective crosslinks (Mc) and wearfactor for copolymers with indicated amount of unsaturations (amount of pendant double bonds per 100.000 C-atoms) and indicated radiation dose.

Conclusions: A new (UHMW)PE grade with low wear levels at 25 kGy & less reaining free radicals was developed by copolymerizing ethylene and 1,7-octadiene.

These new diene-copolymers show a similar network density and wear resistance as highly crosslinked material (75 kGy) after only a sterilization dosage (25 kGy) of γ radiation. The reduced remaining free radical content will most probably result in a more oxidatively stable material, which potentially eliminates the need for remelting after crosslinking. This should also give the copolymers improved mechanical properties as compared to current HXLPE grades after remelting. The mechanical properties and the oxidative stability are currently being studied in more detail.

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