

UHMWPE: Effect of Gamma Radiation on the Cross Linking and Oxidative Behaviour studied with the Chemiluminescence Approach.

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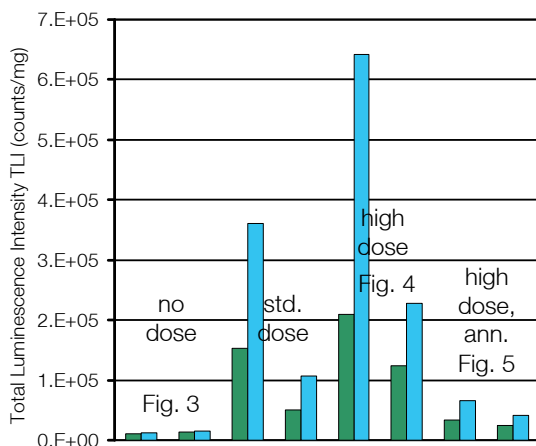
INTRODUCTION: Ultra high molecular weight polyethylene (UHMWPE) is a subset of the thermoplastic polyethylene. It has extremely long chains, with molecular weight usually between 2 and 6 million. The longer chains serve to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This results in a very tough material, with the highest impact strength of any thermoplastic presently made. It is highly resistant to corrosive chemicals, with exception of oxidizers. It has extremely low moisture absorption, has a very low coefficient of friction, is self-lubricating, and is highly resistant to abrasion. It is odorless, tasteless, and nontoxic.

Due to these properties, UHMWPE is used over 40 years as a successful biomaterial in hip, knee, and most recently, spine implants. Throughout its history, there were unsuccessful attempts to modify UHMWPE to improve its clinical performance; one attempt is the cross linking by gamma or electron beam radiation since the late 1990s.

The high energy radiation treatment leads UHMWPE susceptible to oxidative decay, due to the formation and accumulation of radical species in the polymer matrix.

METHODS: The susceptibility of UHMWPE against cross linking and oxidation was studied with the Chemiluminescence (CL) method. Degradation of hydrocarbon polymers involves a radical chain reaction, which propagates in the presence of oxygen. The CL emission mechanism arises from the phosphorescent relaxation of a triplet carbonyl species, formed in a bimolecular termination reaction by the Russell mechanism or by direct hydroperoxide decomposition (Fig. 1). The CL-data were measured with a 1¹⁰ basic configuration from ACL Instruments (Fig. 2). All samples were characterized at isothermal condition (37°C); after 24h in nitrogen (4N), the atmosphere was switched to synthetic air for additional 24h.

UHMWPE discs (dia 15mm) in different variations were supplied by Dr. Lukas Eschbach, Robert Mathis Foundation RMS (Bettlach CH): applied doses were 0Gy, 25..37kGy and 75..111kGy, each of them not stabilized and stabilized (Vitamin E). Additionally parts of the high dose irradiated samples were annealed to accelerate the cross linking reaction after gamma irradiation treatment.



RESULTS: The CL-data are visualized in Fig. 2, 3, 4 and the calculated Total Luminescence Intensity (TLI = integrated CL-emission) for the nitrogen and air segment are presented in Tab. 1.

Tab. 1: TLI values of the different UHMWPE samples.

DISCUSSION & CONCLUSIONS: The CL emission study indicates the following behavior: The cross linking effect due to the gamma irradiation treatment clearly appears in inert gas atmosphere at low temperature where the TLI is multiple times higher on the irradiated samples than on not irradiated samples. In the oxidizing environment, the TLI values of gamma irradiated samples increase dramatically. The stabilization of UHMWPE with Vitamin E increases the susceptibility to cross linking but also to the oxidation when exposed to Gamma radiation dose. On the other hand, the not irradiated, not stabilized samples are less stable against oxidation compared to the stabilized samples.

It is to be assumed that the gamma radiation results to deleterious susceptibility of UHMWPE against oxidation and to an accumulation of radical species in the matrix which may react later in undesired pathways.

The damage by oxidation depends on the radiation dose and stabilisation. Already the dose used for the sterilization of the material makes the UHMWPE susceptible to oxidation damage.

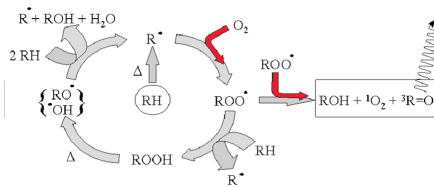


Fig. 1: The emission of light during the oxidative degradation process of organic substances is a part of the reaction course. Chemiluminescence is normally attributed to a transition of excited triplet-carbonyl-function (³R=O*) into its ground state: simplified autoxidation scheme of organic substances (left-hand side) and the Russell mechanism (right-hand side).



Fig. 2: 1¹⁰ basic instrument configuration with highest sensitivity enables the precise characterization of sample sizes up to 22mm diameter. The basic instrument configuration may be easily addressed at any time by upgrading with innovative hardware modules.

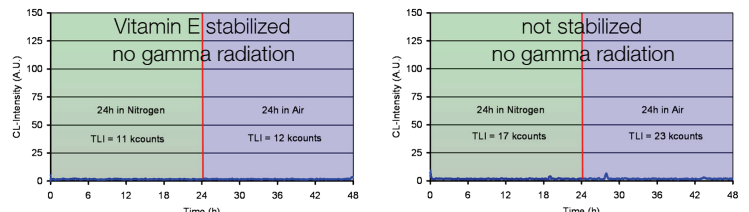


Fig. 3: CL-emission of untreated (0Gy) UHMWPE in nitrogen (green part) and in synthetic air atmosphere (blue part): comparison of the Vitamin E stabilized (left-hand side) and not stabilized sample (right-hand side).

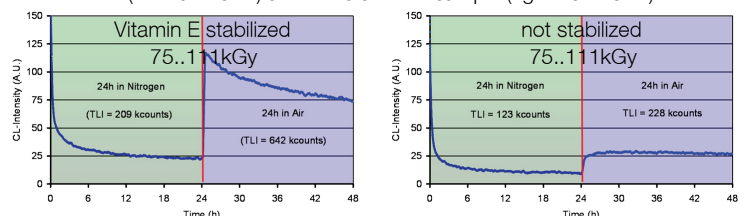


Fig. 4: CL-emission of gamma radiation treated (75..111kGy) UHMWPE due to cross linking in nitrogen (green part) and due to a combination of cross linking and oxidation in synthetic air atmosphere (blue part): comparison of the Vitamin E stabilized (left-hand side) and not stabilized sample (right-hand side).

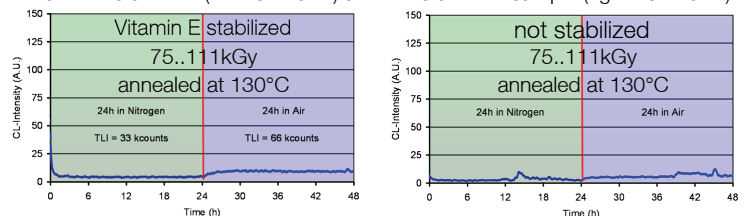


Fig. 5: CL-emission of gamma radiation treated (75..111kGy) and annealed UHMWPE in nitrogen (green part) and in synthetic air atmosphere (blue part). It is obvious, that the annealing procedure reduces the cross linking and oxidation effect compared to the un-annealed sample (Fig. 4 left hand side).