HINDERED AMINE LIGHT STABILIZERS:
A (BETTER) ALTERNATIVE FOR RADIATION CROSS-LINKED UHMWPE IMPLANTS

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Introduction
To decrease wear, nowadays UHMwPE implants are cross-linked using γ or EB radiation [1]. However after radiating the polymer, long living radicals are still present, which can initiate the oxidation of the polymer and lead to a reduced life time [2]. This undesired process can be prevented in different ways. To reduce the residual radical concentration the polymer can be heated. To be effective it has to be heated to above its melting point, which results in a decrease of crystallinity and thus the properties. When the polymer is heated to just below its melting temperature not all radicals are trapped [1,3]. Another method to reduce the residual amount of radicals is by applying radical scavengers of which Vitamin E is the most well known. However, applying Vitamin E has several disadvantages. The main disadvantages is that this antioxidant already reacts with radicals during the cross-linking process leading to a reduced radiation efficiency and a consumption of (a part of) the dosed amount [3]. In this presentation alternative stabilizers are presented that do not have these disadvantages.

Experimental

Materials
The UHMwPE used was MG003 from DSM (Mw 7.3 million g/mol). The stabilizers used are Vitamin E (from DSM Nutrional Products) Chimassorb® 944, Chimassorb 119 and Tinuvin NOR 371 (from Ciba Specialty Chemicals). For their chemical structure see Fig 1. The stabilizers were added to the polymer by solution blending of the stabilizer in a for the stabilizer appropriate solvent.

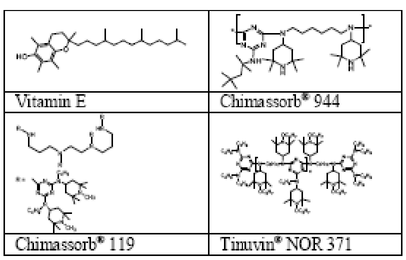
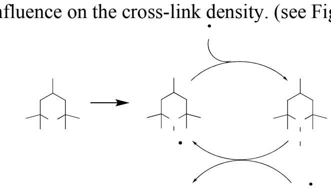


Fig. 1. Chemical structure of used stabilizers

Sample preparation
All powders were compression moulded into sheets according to ISO 11542-2. These sheets were irradiated with 25, 75 and 150 kGy ray (at Beta-Gamma-Services GmbH). The samples dimensions needed for analyses were machined from the moulded sheets. Tensile bars (Type ISO 527-5B) were punched from these 1 mm thick plaques. The cross-link density was determined using 5mm*5mm*5mm cubes

Ageing and analysis
All materials were aged during two weeks in an air venting oven at 110°C. The cross-link density was determined according to ASTM F2214-02. Oxidation indices were determined on coupes of about 100 µm, which were cut from cubes of 5*5*5 mm. according to ASTM F2102-06. The oxidation index was defined as the peak height at 1717 cm^{-1} using a baseline drawn from 1680-1765 cm^{-1}.

Results and discussion
The mechanism of action of HALS stabilizers is different from that of radical scavengers as Vitamin E. In scheme 1 a simplified mechanism of action of HALS stabilizers is given, for more detailed mechanisms see refs. 4 and 5. From this mechanism a high activity of HALS can be expected because it in principle is not consumed
As Vitamin E reacts with alkyl radicals it interferes in the cross-linking and it is (partly) consumed during irradiation of the sample. This results in a decreased cross-link density at given radiation dose (see Fig 2). HALS stabilizers themselves do not scavenge radicals; they first have to be converted into a nitroxide, which is the radical scavenger. As this does not happen during radiation, HALS stabilizer doe not have a negative influence on the cross-link density. (see Fig 2).



Scheme 1. Simplified radical scavenging mechanism of HALS Stabilizers

The effectivity of the stabilizers was determined by measuring the change in carbonyl absorbance due to ageing for two weeks at 110°C (Fig 3). For the unstabilized samples the carbonyl absorbance was over 10 (not shown). For all the other samples it was comparably low, showing that at a concentration of 500 ppm the used HALS stabilizers are as effective as Vitamin E at a concentration of 1500 ppm.

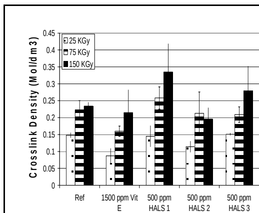


Fig 2. Influence of stabilizer type on cross-link density after radiation with different doses

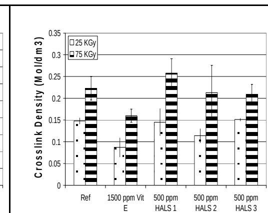


Fig 3 Influence of stabilizer type on the carbonyl absorbance after two weeks at 110°C in an oven

Conclusion
At the moment Vitamin E is the state of the art in stabilizing UHMwPE implants. However this stabilizer has some drawbacks. It has a negative influence on the cross-linking, leading to a lower cross-link density, a (partly) conversion of Vitamin E. These drawbacks can be overcome by using HALS stabilizers, which makes this class of stabilizer potentially better suitable for these applications.

References

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