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Hindered amine light stabilizers: An alternative for radiation cross-linked UHMwPE implants

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ABSTRACT

To reduce wear UHMwPE implants are commonly cross-linked by use of gamma or e-beam irradiation. After irradiation however, radicals are still present that may cause oxidative degradation of the polymer. A way to reduce oxidative degradation could be to add a stabilizer to the polymer. Currently Vitamin E is the state of the art in stabilizing irradiation cross-linked UHMwPE implants. However, this stabilizer has some drawbacks. It interferes with the cross-link chemistry, leading to a lower cross-link density, it will be consumed and it results in the discolouration of the UHMwPE compound due to Vitamin E conversion products. It has been shown that all these drawbacks can be overcome by using HALS stabilizers. Due to their different mechanism of action, HALS stabilizers do not interfere with the cross-link chemistry. As part of the stabilization mechanism the radical scavenging molecules are actually regenerated, which allows for using a lower total concentration. The HALS conversion products do not result in discoloration of the polymer compound. Although their biocompatibilities still have to be evaluated, HALS stabilizers are potential alternative stabilizers for UHMwPE implants.

1. Introduction

Due to its excellent wear resistance and low friction coefficient, Ultra High Molecular Weight Polyethylene (UHMwPE) is successfully applied in hip and knee replacements since the 1960s [1]. Nonetheless, one of the most common complications of the use of UHMwPE and the leading reason for revision is osteolysis [2,3], which is attributed to UHMwPE wear particles [4]. As a result major research efforts were directed to reduce wear rates. It was found that cross-linking UHMwPE implants using Gamma or Electron Beam (EB) radiation leads to a significant decrease of wear rates [5]. Consequently, radiation cross-linked UHMwPE has become today's gold standard in the design of artificial joints.

EB and Gamma rays have an energy that is some orders of magnitude higher than bond scission energies of C–C and C–H bonds. As a result EB and Gamma irradiation of UHMwPE leads to cleavage of these bonds leading to hydrogen as well as primary and secondary alkyl radicals. The formed alkyl radicals can react with each other or with unsaturations being present in the polymer leading to cross-linking of the polymer. According to Bracco et al. [6] the addition of alkyl radicals to vinyl end groups is the most likely reaction. Radicals formed during irradiation are present in the amorphous and crystalline phase. Those in the amorphous phase will relax within 3–10 h [7], however those in the crystalline phase were shown to be present even after storage for 8 years [8].

If the polymer after irradiation comes into contact with air the remaining alkyl radicals will initiate the oxidation of the polymer, which leads to a reduction of properties [9,10] and possible premature failure of the UHMwPE implant. This undesired oxidation process can be prevented in different ways. To reduce the residual radical concentration the polymer can be heated. To be effective the polymer has to be heated to above its melting point; however, this post-irradiation melting step reduces the mechanical properties and fatigue strength of irradiated UHMWPE [11]. When the polymer is heated to just below its melting temperature not all radicals are quenched [5,12].

Another method to reduce the residual amount of radicals is by applying radical scavengers, of which Vitamin E is the most well known. There are two methods of incorporating this stabilizer into UHMwPE. One is to blend Vitamin E with polymer powder prior to consolidation followed by cross-linking using ionizing irradiation. However, in this way applying Vitamin E has several disadvantages.

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The main disadvantages are that the antioxidant already reacts with radicals during the cross-linking process leading to a reduced radiation efficiency or cross-link density and a consumption of (a part of) the dosed amount of stabilizer [12–14]. Another problem is that in the presence of Vitamin E the polymer becomes yellow. It was shown that in the body Vitamin E is recycled [15], so that in the body the amount of decomposition products is limited. This is not the case when Vitamin E is used in polymers. In this case the Vitamin E is consumed and several products are formed that are not expected to be formed in the body [16]. Some of the decomposition products of Vitamin E are coloured, which is the reason that polymers containing Vitamin E become yellow. Kurtz et al. [17] investigated two UHMwPE types containing different Vitamin E amounts and showed that there is no relation between the colour of the UHMwPE and the amount of Vitamin E present. This is because the final colour largely depends on the way the material is processed, which is very difficult to control. Although colour is in principle for implants an aesthetic problem, consistency of the colour might be a problem, because it is difficult to argue that the performance of two differently coloured articles is the same.

A second method to apply Vitamin E is by diffusing the stabilizer in the UHMwPE after cross-linking. Obviously in this way incorporated Vitamin E does not have an influence on the cross-linking process. However, to get a homogeneous Vitamin E distribution a two-step diffusion process at elevated temperatures (below the melting point) is necessary. This process involves doping of UHMWPE by soaking in Vitamin E and subsequently homogenization at an elevated temperature [18]. Although in this way incorporating Vitamin E does not show the negative aspects of pre-irradiation incorporated Vitamin E, it is from a production point of view not favoured, as it is much more complicated and time consuming to incorporate a stabilizer in this way than to blend the polymer with the stabilizer.

So there is a need for a stabilizer that can be blended with the polymer before irradiation and that does not show the negative aspects as described for Vitamin E. Hindered Amine Light Stabilizers (HALS) might be a class of stabilizers that show such behaviour. In this paper a comparison is made between consolidated and cross-linked materials made from UHMwPE powder doped with Vitamin E and several HALS stabilizers.

2. Experimental

2.1. Materials

The investigated types of UHMwPEs are MG003 from DSM (molecular weight: 7.3 million g/mol) (UHMwPE-1) and GUR 1020 (molecular weight; 3.5 million g/mol [19]) from Ticona (UHMwPE-2). The stabilizers used are Vitamin E (from DSM Nutritional Products), and the oligomeric or high molecular weight hindered amine light stabilizer (HALS) Chimassorb® 944, Chimassorb® 119 and Tinuvin® NOR 371 (from Ciba Specialty Chemicals). For their chemical structure see Fig. 1. From the hindered amine light stabilizers Chimassorb 944 is FDA regulated (up to 0.3 wt %) for use in polyethylene that is intended to come in contact with food applications [20].

2.2. Sample preparation

The stabilizers were added to the polymer powders by solution blending of the stabilizers in isopropanol (from Aldrich). Solutions of the different stabilizers were mixed in a 1:1 weight ratio with the polymer, followed by evaporation of the solvent overnight at lab conditions and drying of the powder at 40 °C at reduced pressure during 24 h. All prepared samples are shown in Table 1.

All these powders were compression moulded into 15 mm thick sheets (according to ISO 11542-2). These sheets were gamma irradiated with 25, 75 and 150 kGy (at Beta-Gamma-Services GmbH). The samples dimensions needed for analyses were machined from the corresponding moulded samples. Colour and FT-IR measurements were done on 1 mm thick plaques. Tensile bars (Type ISO 527-5B) were punched from these 1 mm thick plaques. The cross-link density was determined using 5 mm × 5 mm × 5 mm cubes.

2.3. Ageings and analysis

The materials based on UHMwPE-1 were aged during two weeks in an air venting oven (Binder FDL115) at 110 °C. The UHMwPE-2 compounds were aged during six weeks at room temperature.

The swell ratio of the different samples was determined from the increase in height of 5 × 5 × 5 mm cubes in o-xylene at 130 °C using an SRT-3 Unit (Cambridge Polymer Group), in triplicate (in compliance to ASTM F2214-02). The swell ratio was computed from the cubed ratio of the transient sample height *H* normalized by the initial height *H0*.

Colour measurements were done in reflectance including UV light and the specular component (gloss). The measurements were done on areas of 8 mm. As light source a Xenon lamp was used and as aperature a 10° field of view. The samples were illuminated under an angle of 8°. As colour coordinates L*, a* and b* (CIELAB, D65, 10°, d8) were used, in which L* reflects the black–white axis, a* the red-green axis and b* the blue–yellow axis. The used method is in compliance to ISO 7724-1-2-3. All measurements were done in triplicate showing deviations smaller than 0.1%. As yellowing results in an increase in b* and in this study yellowing of the samples was most important, increases in b* are shown relative to a non irradiated not aged sample (∆b*).

The changes in tensile strength and elongation at break were determined using dumbbell-shaped tensile bars (Type ISO 527-5B) which were stamped from 1 mm thick plaques. These measurements were done in accordance with ISO-527 using a Zwick 1445. The clamp speed during the tensile test was 50 mm/min. All determinations were done at least in triplicate.

The FT-IR measurements were performed on a Perkin Elmer Spectrum One spectrophotometer with a resolution of 4 cm^{-1} and 16 scans per spectrum. The carbonyl index was determined from the absorption at 1718 cm^{-1} (peak height) using the absorption at 2020 cm^{-1} (peak height) as a reference and defined as the absorbance at 1718 cm-1 divided by the absorbance at 2020 cm^{-1} [21]. The data are presented as the increase of the Carbonyl index relative to the not aged samples (Delta Carbonyl Index)

3. Results

The influence of irradiation and ageing on differently stabilized UHMwPE-1 (unstabilized, 1500 ppm Vitamin E and 500 or 1500 ppm of HALS-1, HALS-2 or HALS-3) and UHMwPE-2 (500 or 1500 ppm of Vitamin E or HALS-1) were determined using swell ratio, carbonyl absorption, mechanical properties and colour measurements before and after ageing. In the following paragraphs all results are presented.

3.1. Ageing of differently stabilized irradiated UHMwPE

3.1.1. The increase in carbonyl absorbance

Stabilizers were applied to decrease the oxidation rate after irradiation. In the following the influence of the different stabilizers on the increase of the carbonyl index are depicted.

For the UHMwPE-1 compounds the effectivity of the stabilizers was determined by measuring the change in carbonyl absorbance due to ageing for two weeks at 110 °C (Fig. 2). For the unstabilized samples the carbonyl index was after ageing for all irradiation dosages more than 3 (not shown). Although there was a slight increase with irradiation dose the increase in carbonyl index was in comparison to the unstabilized UHMwPE very low. The HALS stabilizers were very effective in reducing the increase of the carbonyl index. Even at a concentration of 500 ppm the used HALS stabilizers were as effective in preventing oxidation as Vitamin E at a concentration of 1500 ppm.

For the UHMwPE-2 compounds the effectivity of the stabilizers was determined under more realistic conditions. In this case the change in carbonyl absorbance due to storage during six weeks at room temperature was determined (Fig. 3). As a result of ageing at room temperature the unstabilized UHMwPE-2 compound showed an increase of the carbonyl absorbance. As expected the influence of storage time on the increase of the carbonyl absorbance increased with irradiation dose. Addition of 500 ppm Vitamin E, before irradiating the compounds, led to a small decrease in oxidation rate. This improvement was larger when 1500 ppm