INDRODUCTION:

The oxidation of ultra-high molecular weight polyethylene (UHMWPE) implants has been widely studied and reported in literature. One way to increase the oxidation resistance of conventional and radiation crosslinked UHMWPE is to stabilize the material with the natural antioxidant vitamin E (1). Other synthetic antioxidants can also be used to stabilize UHMWPE against oxidation. A technical stabilizer system widely used for polyethylene is represented by the Irganox® family and it can be obtained with different number of hinder phenols per molecule.

In this paper we examined the thermal oxidative stability of UHMWPE blended with Irganox 1010, 1035 and 1076 (with 4, 2, and 1 hindered phenol per molecule, respectively) as a function of irradiation dose and stabilizer concentration. The aging experiments were carried out in air at 120 °C with thin films. Vitamin E is known to be partially degraded and to be grafted onto the UHMWPE chains by the high energy irradiation during crosslinking (2); the extent to which these happen with Irganox has not been reported. Therefore we also investigated Irganox degradation and grafting to UHMWPE chains.

METHODS:

Pucks of UHMWPE (diameter: 10.5 cm, thickness: 1 cm, GUR1050) containing Irganox 1010, 1035 and 1076 were prepared by blending UHMWPE powder with Irganox (0.02, 0.1, 0.5, and 1.0 wt%) and consolidating the blends. The blends were irradiated by electron beam to 100 and 200 kGy (MIT, Cambridge, MA) in argon. Thin sections (150 µm) were cut from the middle of the pucks for accelerated aging experiments. The UHMWPE films were held with glass pipettes in an oven at 120 °C in air. Fourier Transform Infrared (FTIR) Spectroscopy analysis was performed on the thin sections in timed intervals with a FTIR microscope (Bio-Rad FTS155/ UMA500, Natick MA). Two films were used for each sample and 3 spectra were measured in the middle of each film in timed intervals (aperture size: 100x100 µm², distance between measurement points on each film: 2 mm); after the measurements the films were put back in the oven.

The infrared spectra were analyzed to calculate the Irganox concentration (OH-peak area at 1235 cm⁻¹, trans-vinylene index (peak area at 965 cm⁻¹) and crystallinity (peak area at 1303 cm⁻¹). All peaks were normalized using the polyethylene skeletal absorbance peak area at 1895 cm⁻¹. Oxidation indices were calculated as the ratio of the areas under the carbonyl absorbance at 1720 cm⁻¹ to the absorbance over the methylene absorbance at 1380 cm⁻¹.

Thin sections (150 µm) were cut from the middle of the pucks to assess the extent of Irganox grafting. The films were extracted in boiling hexane for 16hrs. Irganox concentration was determined before and after the extraction by means of FTIR.

RESULTS:

Fig 1 shows the oxidation of the thin films with 0.1 % stabilizer in air at 120 °C as a function of aging time, Irganox type and radiation dose. Irganox 1010 yielded the highest thermal oxidation resistance, followed by Irganox 1035 and 1076. Irganox 1010 has the highest OH-group concentration per gram (stabilization potency) and the highest molecular mass (reduced migration).

Compared to samples with 0.1 % vitamin E (1), the oxidative resistance of the Irganox samples was remarkably higher (0.1% VitE / 0 kGy: oxidation onset: 196 h; Irg.1076: 1020 h; Irg.1035: 1420 h; Irg.1010: 2340 h). With vitamin E a similar stabilization efficiency can only be realized at higher concentrations. The Irganox concentration in the films decreased slowly with time for all three Irganox types following a linear trend (R² Irg.1010: 0.874).

Fig. 2 shows the results of the extraction experiments of the 1% samples. Similar to vitamin E (2), fractions of Irganox were grafted onto the UHMWPE chains by irradiation. Irg.1010 and 1035 showed a very similar grafting tendency and the grafted fraction of Irg.1076 was lower than that of 1010 (Irg.1010 / 200 kGy: 46.5±1.9 %; Irg.1076 / 200 kGy: 38±5.5 %). The grafted fractions of the 0.5% samples increased faster with radiation dose, reaching a plateau of approx. 80 % at 150 kGy. The stabilizer degradation caused by irradiation was the lowest for Irg. 1010 (1% Irg.1010: 23.3±1.9%; 1% Irg.1035: 39.3±5.1 %; 1% Irg.1076: 65±1.5%).

CONCLUSION:

All Irganox samples showed higher stabilization efficiency than that measured with vitamin-E. We postulate that this was likely due to slower loss of the antioxidant from the thin films during aging with the larger Irganox molecules. The 1076 has a molecular structure and size similar to that of vitamin-E. Therefore a higher diffusion of vitamin-E is hindered phonel per molecule, respectively) as a function of irradiation dose and stabilizer concentration. The aging experiments were carried out in air at 120 °C with thin films. Vitamin E is known to be partially degraded and to be grafted onto the UHMWPE chains by the high energy irradiation during crosslinking (2); the extent to which these happen with Irganox has not been reported. Therefore we also investigated Irganox degradation and grafting to UHMWPE chains.

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RESULTS:

Fig 1 shows the oxidation of the thin films with 0.1 % stabilizer in air at 120 °C as a function of aging time, Irganox type and radiation dose: oxidation of the thin films with time showed a step function where the onset of oxidation time was in general longer with decreasing radiation dose. Irganox 1010 yielded the highest thermal oxidation resistance, followed by Irganox 1035 and 1076. Irganox 1010 has the highest OH-group concentration per gram (stabilization potency) and the highest molecular mass (reduced migration).

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