

Analysis of degradation in UHMWPE a comparative study among the various commercial and laboratory grades UHMWPE

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Abstract. Oxidative degradation of the ultra-high molecular weight polyethylene (UHMWPE) limits the life of implants. This degradation can be monitored to estimate the service life of UHMWPE following the standard protocols as defined by American Standards for Testing Materials (ASTM). In this work, a comparative study has been carried on two commercially available UHMWPE grades i.e. GUR 1020 and GUR 1050 and one laboratory grade UHMWPE which was purchased from Sigma Aldrich. These powder samples were pressed while using hot press with controlled heating and cooling setup in open air under 200 bar of external pressure. These sheets were then subjected to accelerated aging in an oven at 80 °C for three weeks. The degradation of the UHMWPE was monitored by ATR-FTIR technique for three weeks. The oxidation index (OI) measurement showed that the commercial grade UHMWPE i.e. GUR-1020 and GUR-1050 degrade more as compared to laboratory grade UHMWPE. The values of OI after three weeks of accelerating aging were found 0.18, 0.14, and 0.09 for GUR-1020, GUR-1050, and Sigma Aldrich, respectively. In addition to this, it was found that commercial grades of UHMWPE suffer more structural alterations as compared to laboratory grade one. We hope that these results will be of particular and fundamental importance for the researchers and orthopaedic industry.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) belongs to polyolefin family which was introduced after the failure of polytetrafluoroethylene (PTFE) in 1962 by Sir John Charnley. UHMWPE has been used in a number of specific areas including bearing components, gears, sporting goods, guide rails and as a biomaterial in total joints replacement. More than 90% of the total joints replacement cases, hip cups and knee inserts are made of UHMWPE for immediate pain relief in aching patients [1-3]. Artificial joint substitution in elder people has been increasing in accordance with their desire for independent living and recovery of functional use. The Swedish Hip Arthroplasty Register (SHPR) which becomes active in 1979 has recorded types of prosthesis, factors concerning the operation and result in the form of complications. The Nordic Arthroplasty Register Association (NARA) has awarded a major grant from Nordic Council of Ministers in order to harmonize the generic descriptions of the used prosthetics in the region. According to SHPR Annual Report 2013,



16,299 total hip replacement operations were operated in Sweden which corresponds to 324 per 100,000 inhabitants aged 40 years or older. International comparison of the countries reporting shows that Sweden has among the highest incidence means life expectancy is increasing and proportion of older people among the population increases [2]. In case of knee joint substitution, average life of UHMWPE joint is 15-20 years and life of an artificial joint depends on the degree of deterioration of UHMWPE. Bio-implant materials such as acetabular liners and tibial inserts are made from UHMWPE because of having biocompatibility, high wear resistance, lower coefficient of friction, suitable stiffness, abrasion resistance, toughness and relative low cost [4]. The extremely high viscosity of UHMWPE has made a challenging task in processing of reinforced UHMWPE composites. UHMWPE is almost impossible to process in the melt because of their high melt viscosity. Much effort has done in finding suitable processing methods [5]. In addition to this researchers are working to find the suitable method for stopping the degradation of UHMWPE by incorporating antioxidants, nano fillers, silane etc. [6]. However, some laboratories are using various available grades of UHMWPE which include commercial grades i.e. GUR-1020, GUR-1050, and some are using laboratory grade UHMWPE while purchasing from different suppliers of chemical industry. It is therefore, a comparative study among commercial and laboratory grades UHMWPE is necessary for having better understanding of degradation mechanism of UHMWPE.

In this work, a comparative study has been carried on two commercially available UHMWPE i.e. GUR 1020 and GUR 1050 and one laboratory grade UHMWPE purchased from Sigma Aldrich. These samples were subjected to accelerated aging for three weeks following the standard protocol as defined by ASTM standards [1]. The structural changes and oxidation degradation of these samples has been monitored by ATR-FTIR spectra taken after each week.

2. Materials and methods

2.1 Sample preparation

The UHMWPE (GUR 1020, GUR-1050, and Sigma Aldrich) was pressed into the sheets of 1mm thickness using hot press 190°C at 20MPa. A hold time of 10 minutes was given. After compression treatment samples were cooled down to room temperature at 20MPa. The samples were then divided into four groups, one was kept as non-aged sample and other three samples were put into oven for one, two and three weeks for accelerated aging, respectively at 80°C in air following ASTM standard guide (ASTM F2003-00) [1]. The UHMWPE which was purchased from Sigma Aldrich was labeled as 'S' in the manuscript from here on.

2.2 Ftir measurement

The absorption of electromagnetic energy in the infrared (IR) region occurs due to vibrational modes of atoms in solids and liquids. Chemical species having different molecular formula are present in semi-crystalline materials such as polymers. FT-IR spectroscopy is extensively used experimental technique for the investigation of molecular structures of polymers. It also investigates chemical bonds. Nicolet-6700 Fourier transform infrared spectrophotometer (Thermo Electron Corporation, Waltham, MA, USA) was used to record IR spectra in attenuated total reflectance mode and plotted in transmission mode. The spectra were obtained in the range of 4000 cm⁻¹ to 500 cm⁻¹ at a resolution of 6 cm⁻¹ after acquiring 216 scans. The irradiated compressed sheets were served as protection for measurements after receiving from irradiation department. The spectra for all samples were recorded from three/four points and then averaged to decrease signal to noise ratio (SNR).

3. Result and discussion

The most effective way to accelerate the ageing of UHMWPE currently in practice is oven aging and researchers are using this method for estimating the service life of UHMWPE and its composites [3-4]. Un-aged and aged samples are tested using FTIR spectrometer on the recommended setting as mentioned above. The IR absorption bands of particular interest as far as degradation of these commercial and laboratory grade UHMWPE is concerned are listed in the Table 1.

Table 1. UHMWPE IR absorption bands of our interest

Description	IR absorption band (cm ⁻¹)
Alcohol & hydro-peroxide	3450-3350 [7-8]
Carboxylic acid, Aldehydes, ketones & Carbonyl species	1710-1740 [7-8]
Ethers and other -C-O-C groups	1100-1400 [7-8]
Trans-vinylene groups, C=C Unsaturated bonds	800-1000 [7-8]

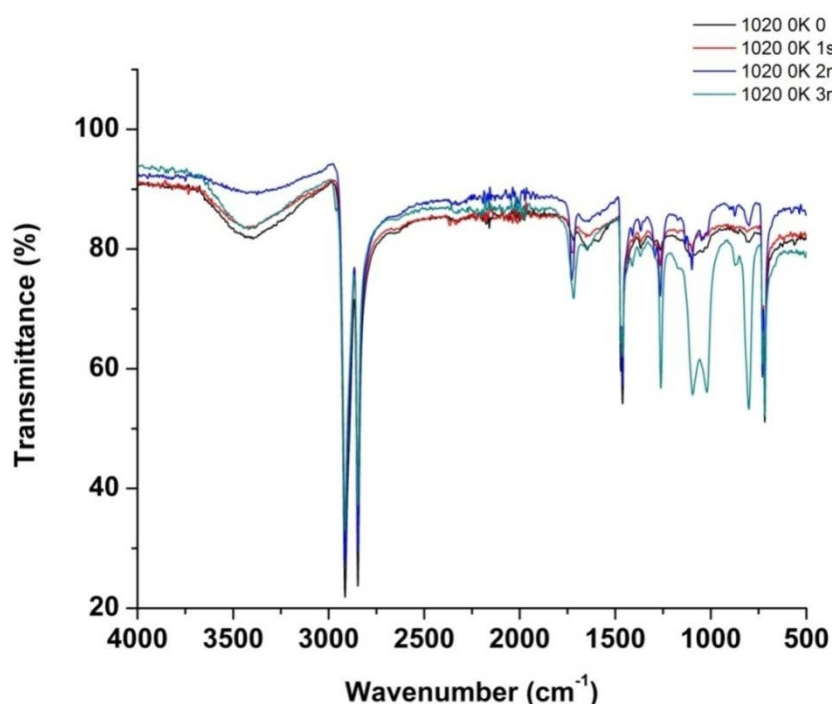
**Figure 1.** FTIR spectra of GUR-1020 grade of UHMWPE

Figure 1 show FT-IR spectra of sheets of UHMWPE prepared from GUR-1020. In the figure, it can be seen that each spectrum is labeled as 1020-0K-xW, where variable 'x' represent the time of oven aging i.e. it is 0 for control samples, 1 for one week aged, and so on up three weeks. It can be seen from the figure that spectra of GUR-1020 show an increase in absorption in the following bands after aging.

- Form 3000 cm⁻¹ to 3750 cm⁻¹ which corresponds to typical end products of polyethylene (PE) oxidation i.e. hydrogen bonded and non-bonded hydro-peroxide
- Form 1650 cm⁻¹ to 1850 cm⁻¹ which is due to absorption of carbonyl species i.e. C=O
- Form 1460 cm⁻¹ to 1480 cm⁻¹ and 2880 cm⁻¹ to 3000 cm⁻¹ which is associated with PE crosslinking
- Form 1100 cm⁻¹ to 1400 cm⁻¹ which is associated with -C-O-C- vibrations
- Form 800 cm⁻¹ to 1100 cm⁻¹ which is related with the absorption due to C=C un-saturation

It is evident from figure that in addition to increase in absorption due to material degradation, there is significant increase in absorption from 800 cm⁻¹ to 1400 cm⁻¹ which is mainly associated with -C-O-C- vibrations and C=C unsaturation. Furthermore, there is abrupt increase in the absorption of functional groups associated with these bands for three week aged samples. When all chemical groups are investigated, a similar trend has been observed that is hydroperoxides, carbonyl and vinylenes

species have represented considerably higher content for longer aging time. There are no considerable contents are there for control and one week aged samples and found to increase remarkably as the aging time proceeds.

Shown in Figures 2 and 3 are the FTIR spectra of samples prepared from GUR-1050 and Sigma Aldrich grades of UHMWPE. The major changes are almost similar as mentioned above for GUR-1020. However, one can see from Figures 2 and 3 that except from the typical oxidation products and carbonyl species, absorption due to -C-O-C- vibrations and C=C unsaturation have considerable lower values. This fact suggests that GUR-1050 and Sigma Aldrich UHMWPE is more stable as compared to GUR-1020 when subjected to accelerated aging. The lower molecular weight and smaller chains of GUR-1020 might be responsible for this fact. However, further studies are in progress for detail investigation of this difference as far as stability of various UHMWPE grades is concerned.

Now coming to the quantitative measure of UHMWPE degradations due accelerating aging and for this purpose oxidation index (OI) of each sample was calculated following the standard protocol as defined in literature [7-8]. Basically, OI is the ratio of the peak height due to C=O stretching ($^{\circ}\text{C=O}$) components of ketone present at 1718 cm^{-1} to the absorption band at 2020 cm^{-1} which belongs to CH_2 bending vibrations (internal standard, $^{\delta}\text{CH}_2$, “twist” bend) i.e.

$$\text{OxidationIndex(OI)} = \frac{I_{1718}}{I_{2020}}$$

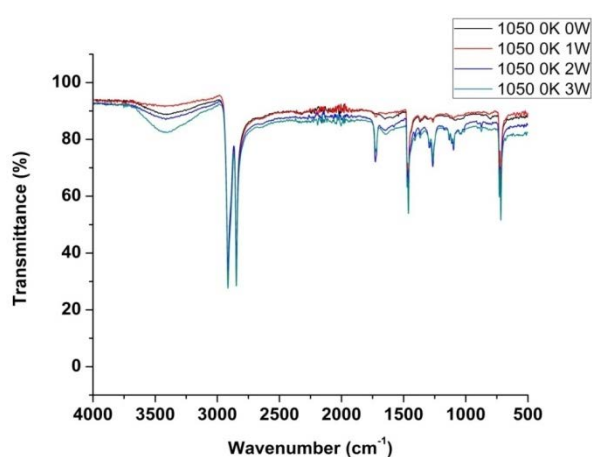


Figure 2: FTIR spectra of GUR-1050 grade of UHMWPE

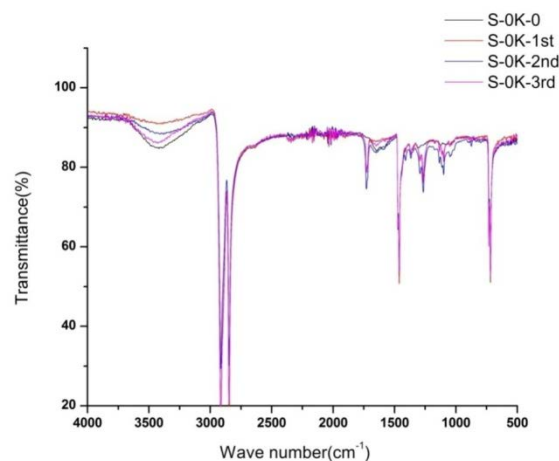


Figure 3: FTIR spectra of UHMWPE samples purchased from Sigma Aldrich

The values of OI are shown in Table 2 below:

Table 2. Oxidation Index (OI) of UHMWPE grades under investigation

UHMWPE Grade	Control	1-week aging	2-week aging	3-week aging
GUR-1020	0.02	0.10	0.13	0.18
GUR-1050	0	0.05	0.13	0.14
Sigma Aldrich	0.01	0.04	0.08	0.09

From figure it can be seen that, the value of OI index is almost zero for control samples, and found to increase with oven aging along with steep rise with increases in aging time. As expected all three grades i.e. GUR-1020, GUR-1050, and Sigma Aldrich have shown maximum values after 3rd week of aging. However, GUR-1020 is found to suffer more after three weeks of aging which 18 % and

degradation in UHMWPE which is purchased from Sigma Aldrich is found less than 10 %. These quantitative results further confirm that UHMWPE which is purchased from Sigma Aldrich (also used at laboratory scale for research work) is more stable when subjected to accelerated aging as compared to GUR-1020 and GUR-1050 which are the commercial products for medical implants. It is therefore, there might be slight difference in the results while using different grades of UHMWPE as far as radiation induced structural changes in UHMWPE.

4. Conclusion

In order to analyze the degradation and thermal stability three different grades (two commercial GUR-1020 and GUR-1050 and one laboratory grade purchased from Sigma Aldrich) were subjected to accelerated aging for three consecutive weeks and tested after each week by using ATR-FTIR spectrometer. The results obtained so far revealed that GUR-1020 suffer more as compared to other two grades i.e. GUR-1050 and Sigma Aldrich. The quantitative analysis showed that GUR-1020 degraded 18%, GUR-1050 degraded 14 %, and Sigma Aldrich UHMWPE degraded less than 10 %, respectively after three weeks of aging. These results showed that UHMWPE which is purchased from Sigma Aldrich and frequently used by researchers in laboratory is more stable when subjected to thermal/accelerating aging.

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