

# Oxidation and Degradation of Polyethylene in Hip Implants

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ANNALS OF TRANSPLANTATION, Vol. 9, No. 1A (Suppl.), 2004, pp. 116–118

## Abstract:

The infrared absorption spectra of polyethylene samples from 13 used acetabular cups from hip prostheses retrieved from patients after different periods of use were studied. The presence of carbonyl compounds was observed in exploited polyethylene samples, confirming progressive oxidative degradation of polyethylene in a biological environment.

**Key words:** Polyethylene Cups; Hip Prostheses; Degradation; Oxidation

## Introduction

The incredibly rapid developments in joint implantation surgery observed in the recent years create a growing demand for biomaterials used in orthopaedics. It is their quality, reliability and biocompatibility that the outcome of the operation and the durability of the implanted joint depend upon. A commonly applied implantation material is ultra-high molecular weight polyethylene, used to produce cups of hip prostheses as well as bearing elements in knee joint prostheses. Used since 1953, this polymer was regarded as a perfect implantation material for years. Its high mechanical resistance, biocompatibility, and, in particular, low price were emphasized. However, many recent reports indicate some significant imperfections of this material, being disclosed especially after its prolonged implantation in a biological environment. Observations of polyethylene cups implanted for different periods show that with time they are subject to visible changes in colour and structure of the bearing surface, indicating chemical changes in the material. Progressive rubbing of the cup internal surface is also observed, leading to considerable wall thinning and deepening of the whole cup. Slits and deep cracks in the load-bearing surface may result over time in the cup fracturing and even completely disintegrating [1-12].

A reason for these changes can be gradual oxidation and progressive polymer degradation. In order to determine the character of the chemical changes in the implanted polyethylene cups, infrared absorption spectra of samples of used polyethylene cups removed from patients during hip joint revision surgery were examined.

## Material and Methods

Endoprotheses made of ultra-high molecular weight polyethylene (Chirulen, ISO) were studied. One series of 8 samples was obtained from new, unused polyethylene cups designed for implantation, the other series consisted of samples from 12 polyethylene cups removed from patients during hip joint revision surgery following different periods of use, ranging from 4 months to 20 years (see Table 1).

Samples were provided for study as chips obtained from new and used polyethylene cups. Pellets containing ca. 60 mg of polyethylene and 800 mg of KBr were prepared from these samples and subjected to spectroscopic measurements. FTIR absorption spectra were recorded using a BRUKER IFS 48 spectrophotometer with a DT detector.

## Results

The obtained FTIR spectra were subjected to initial processing in the range of  $400\div 4000\text{ cm}^{-1}$ , which consisted of the smoothing and adjustment of the basic lines. The spectrum was then normalized according to the reference band with the maximum at  $1468\text{ cm}^{-1}$ , the stretching vibrations of  $\text{CH}_2$  group of  $\text{B}_{2u}$  symmetry [13-15]

The analysis of IR spectra of the samples allowed us to identify groups containing the  $>\text{C}=\text{O}$  bond, which may appear in a different molecular environment and to evaluate the progress of oxidative degradation in the

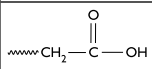
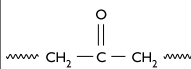
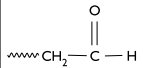
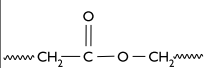
Exploitation time	Series characteristics	Sample name
0	material from new cups and cups exploited for different periods of time	PE(new)
4 months		PE(4m)
22 months		PE(22m)
3 years		PE(3y)
5 years		PE5y
5 years		PE5y
6 years		PE6y
7 years		PE7y
10 years		PE10y
11 years		PE11y
12 years		PE(12y)
15 years		PE(15y)
20 years	PE(20y)	

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**Table 2. Characteristic stretching vibrations of >C=O group in various carbonyl compounds**

	Wave number range [cm <sup>-1</sup> ]	Functional group
	1692 ÷ 1702	carboxylic
	1715 ÷ 1718	ketonic
	1735 ÷ 1741	aldehydic
	1760 ÷ 1767	ester

investigated samples. The ranges of wave numbers at which the bands connected with stretching vibrations of >C=O groups occur are summarized in Table 2 [13-15].

The analysis of the IR spectra of PE samples shows that the material taken from new, unused cups does not reveal any oxidation, but in the used prosthesis spectrum (see for example Fig. 1), a complex band can be observed in the range 1650 ÷ 1800 cm<sup>-1</sup>, which is related to the stretching vibrations of >C=O groups. As it was previously shown [16], the carbonyl band is a superposition of 4 sub-bands, corresponding to ketonic, aldehydic, ester and carboxylic groups, described by the combination of Gaussian (20%) and Lorentzian (80%) functions:

$$G(\tilde{\nu}) = A(\tilde{\nu}) = \frac{1}{\Delta\sqrt{\pi}} \left\{ - \left( \frac{\tilde{\nu} - \tilde{\nu}_{\max}}{\Delta} \right)^2 \right\}$$

$$L(\tilde{\nu}) = A(\tilde{\nu}) = \frac{\Gamma}{\pi} \frac{1}{\Gamma^2 + (\tilde{\nu} - \tilde{\nu}_{\max})^2}$$

The sub-bands were integrated and summed up according to Eq. 1, and this procedure resulted in the evaluation of the integral absorption intensities of sub-bands 1-4,  $I_i$ , and the total integral intensity of carbonyl band,  $I_{C=O}$ .

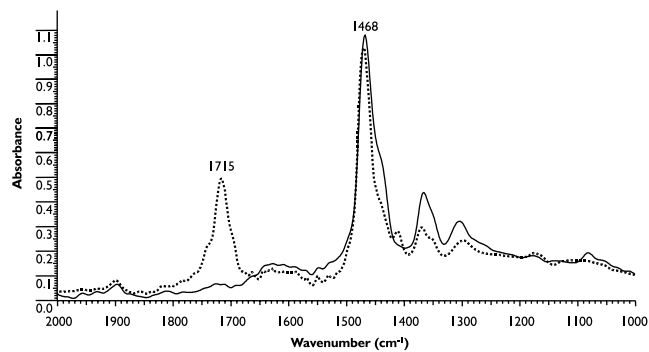
$$I_i = \int I_i(\tilde{\nu}) \cdot d\tilde{\nu} \quad I_{C=O} = \sum_{i=1}^{n=4} I_i \quad (1)$$

The intensities of the sub-bands corresponding to the functional groups containing carbonyl bonds are presented in Table 3.

In order to compare the relative amounts of the four types of carbonyl compounds found in the PE samples, the ratios  $(I_i/I_{C=O}) \cdot 100\%$  were calculated. They are summarized in Fig. 2.

## Discussion

The analysis of the FTIR absorption spectra shows a visible difference in the chemical structure of the samples derived from unused and exploited polyethylene cups. The complex absorption band corresponding



**Figure 1.** FTIR absorption spectra of the samples derived from a new polyethylene cup (solid line) and a cup used for 22 months (dashed line).

**Table 3. Integral intensities ( $I_i$ ) of the constituent sub-bands in the absorption band of polyethylene hip joint endoprotheses after different periods of implantation**

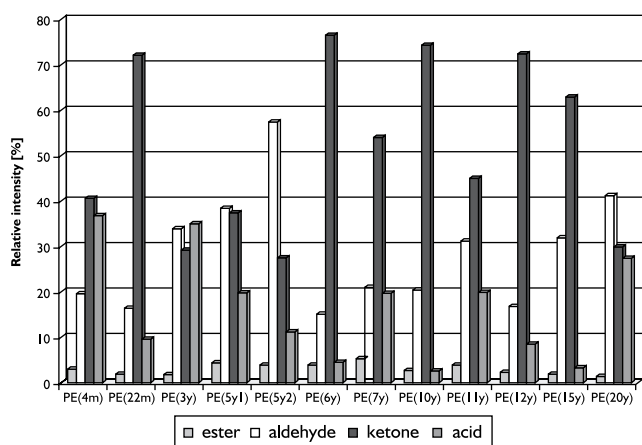
Sample	Sub-band 1** $I_1$ ester	Sub-band 2** $I_2$ aldehyde	Sub-band 3** $I_3$ ketone	Sub-band 4** $I_4$ carboxylic acid	Total integral intensity $I_{C=O}$ ***
PE (4m)	3.1	2.0	4.2	3.8	10.4
PE (22m)	2.6	2.2	10.0	1.3	13.8
PE (3y)	2.6	4.6	4.0	4.8	13.8
PE (5y,1)*	2.9	2.5	2.5	1.3	6.7
PE (5y,2)*	1.6	2.4	1.1	0.4	4.3
PE (6y)	4.6	1.7	9.0	0.5	11.7
PE (7y)	1.2	0.4	1.2	0.4	2.2
PE (10y)	1.6	1.2	4.5	0.1	6.1
PE (11y)	4.4	3.5	5.1	2.2	11.4
PE (12y)	1.1	0.8	3.4	0.4	4.8
PE (15y)	1.1	2.0	4.0	0.2	6.4
PE (20y)	1.5	4.2	3.1	2.8	10.3

\* used polyethylene cups from different patients,

\*\* sub-bands 1-4 correspond to vibrations of carbonyl groups of different frequencies in the following molecular configurations: sub-band 1 (1760 ÷ 1767 cm<sup>-1</sup>) – ester, sub-band 2 (1735 ÷ 1741 cm<sup>-1</sup>) – aldehyde, sub-band 3 (1715 ÷ 1718 cm<sup>-1</sup>) – ketone, sub-band 4 (1692 ÷ 1702 cm<sup>-1</sup>) – carboxylic acid

\*\*\* total integral intensity of C=O carbonyl group

to the four types of carbonyl groups: ketonic, aldehydic, ester and carboxylic were observed in the spectra of samples taken from the cups from the revision procedures. The observed changes undoubtedly result from the oxidation and oxidative degradation of polyethylene. The oxidative degradation may be initiated by various physical and chemical factors (e.g. heat, UV and  $\gamma$  radiation, radicals formed in a living organism due to biochemical processes). The resulting



**Figure 2.** The relative absorption intensities of four types of carbonyl groups (the ratios  $(I/I_{C=O}) \cdot 100\%$ ) for PE samples from cups exploited for various period of time.

polymer radicals  $R^{\cdot}$  easily react with oxygen giving peroxide  $ROO^{\cdot}$  radicals [17]. At the site of propagation reactions, hydroperoxides and different types of carbonyl compounds are formed. Aldehyde type compound formation is accompanied by polymer degradation. One can expect that the oxidation process may be initiated even before the implantation, during production and processing or sterilization and storage. After a hip implantation and introduction of PE into the biological environment, the process of PE deterioration may be additionally intensified in the presence of enzymes or active metabolites catalysing oxidation reactions.

Analysis of the data shows that the integral absorption intensities of the sub-bands related to various carbonyl compounds, the total integral intensity of  $C=O$  group, and the relative intensities of the sub-bands vary with the time of implantation. As shown in Fig. 2, ketone and/or aldehyde structures are the main products of the reaction. The relative intensities were lower for carboxylic groups, and the lowest values were calculated for ester groups. However, no correlation between the integral intensities of carbonyl absorption and the

endoprosthesis usage time was found. Such a visible lack of correlation may result from the fact that the polymer degradation process is a complex phenomenon, simultaneously dependent upon a number of exogenous and endogenous factors, including a unique, individual tissue reaction around the implanted PE cup and the patient's individual immunological reaction. Progressive oxidation-related degradation gradually deteriorates physical and mechanical polymer properties (e.g. hardness, tensile strength), and this may potentially weaken polymer mechanical strength and accelerate the process of mechanical polyethylene cup wear.

The lack of correlation between the degree of degradation and the prosthesis usage time also undoubtedly proves uneven implanted polyethylene wear, which is a consequence of the fact that the aforementioned factors may act in an accidental and uncontrolled way. The accidental character of the oxidation-related polymer degradation process is probably the underlying cause of premature and excessive wear of some polyethylene cups, as described in literature, which cannot be explained solely by mechanical factors.

Therefore, the question remains whether a material in which degradation may proceed in an accidental and uncontrolled way is able to meet any binding standards for mechanical wear as required for medical products. This question should be answered beyond any doubt by the producers and distributors of joint endoprostheses containing polyethylene elements.

## Conclusions

1. Changes in the chemical structure of the material due to oxidative polymer degradation can be observed in polyethylene cups implanted in the human body.
2. There is no simple correlation between the extent of oxidative degradation of the polymer and the endoprosthesis usage time.
3. Excessive oxidation and degradation of the implanted polyethylene may be the reason for premature cup wear in hip joint endoprostheses.

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