JOANNA KOWAL[1)], BARBARA CZAJKOWSKA[2)], ANNA ŻMIHORSKA-GOTFRYD[3)], JANUSZ OTFINOWSKI[2)], ANNA WIĘCEK[1)], ANNA WIERZBICKA[1)], JOANNA WOJEWODA[1)]

Oxidation and degradation of polyethylene cups in hip joint prostheses

Summary — The properties of polyethylene cups of hip prostheses produced by Johnson & Johnson Orthopaedics, De Puy International Ltd. (Great Britain) and Aesculap AG & Co. KG (Tuttlingen, Germany), removed after various times of implantation due to their premature wearing out, were compared by means of the analysis of FT-IR spectra and determination of the hardness and viability of macrophages and osteoblasts. The oxidation of polyethylene was found to be a main reason of Aesculap cups' damages.
Keywords: polyethylene, acetabular cups, wearing, oxidation, hardness.

Most of endoprostheses used in total hip arthoplasty have polymer cups made of ultra high molecular weight polyethylene. Growing number of publications have reported excessive premature mechanical wearing of some polyethylene cups [1—10]. In some cases worn cups showed extensive cracks, delaminations, fractures or even total breaking up. This leads to serious complications requiring the replacement of worn implants. There may be several reasons of premature wear of the polyethylene cups: incorrect implantation of the endoprosthesis, constructional failure of the cup, material failure of the polyethylene. However, in the majority of reported cases an incorrect implantation has been reckoned as the cause of the cup damage. There is a strong possibility that the reason of the damage of PE cups is a failure of the material.

Therefore we decided to examine the samples of polyethylene derived from the new unused cups and from exploited damaged cups (prematurely worn out, cracked or broken) retrieved from the patients at the time of surgery revision.

EXPERIMENTAL

Materials

The two types of PE cups were studied: Johnson & Johnson Orthopaedics, De Puy International Ltd. (Great Britain), in further text — samples C_{JJ}, and Aesculap AG & Co. KG (Tuttlingen, Germany), in further text — samples C_{AE}.

Methods

FT-IR spectra were recorded using EQIUNOX 55 (Bruker) spectrophotometer.

The hardness was measured using Brinell's apparatus according to Polish Standard PN-93/C-89030/01.

The viability of macrophages U-937 and osteoblasts SaOs-2 was determined using the method based on 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium bromide — MTT (Sigma) dye metabolism in the living cells' mitochondria [11].

RESULTS AND DISCUSSION

The analysis of FT-IR spectra of PE samples shows that the material taken from the new, unused C_{AE} cup does not show any oxidation, but all this type samples originating from the exploited cups (the time of implantation ranging from 4 months to 12 years) are highly oxidized (Fig. 1).

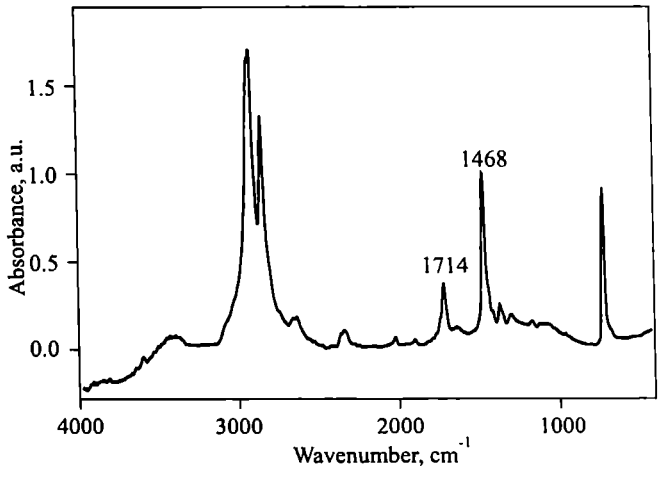

Fig. 1. FT-IR spectrum of C_{AE} sample exploited 4 months

[1)] Jagiellonian University, Faculty of Chemistry, ul. Ingardena 3, 30-216 Kraków, Poland.
[2)] Jagiellonian University, Collegium Medicum, ul. Św. Anny 12, 31-008 Kraków, Poland.
[3)] Rzeszow University of Technology, Department of Plastics Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland.

Figure 2 shows the absorption of the carbonyl band — experimental as well as 4 Gausian-Lorenzian sub-bands. The carbonyl band is complex thus it seemed reasonable to resolve it into sub-bands, taking into account

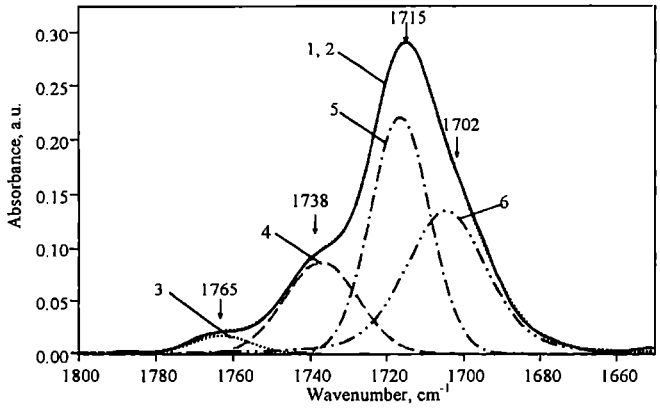

Fig. 2. FT-IR spectra of C_{AE} sample exploited 4 months (see Fig. 1b): 1 — experimental spectrum, 2 — calculated spectrum, 3 — ester band, 4 — aldehyde band, 5 — ketone band, 6 — acidic band. Experimental data and spectrum calculated as a superposition of 4 sub-bands

the literature data referring to the frequencies of C=O groups in oxidized polyethylene: carboxylic (1692—1702 cm^{-1}), ketonic (1715—1718 cm^{-1}), aldehydic (1735—1741 cm^{-1}) and esteric (1760—1767 cm^{-1}) [12]. The sub-bands were integrated and then summed up which allowed to obtain the calculated absorption profile, almost identical with the experimental spectrum (spectra 1 and 2).

The oxidation index (*OI*) was defined as the ratio of the integral intensity of C=O band and the integral intensity of the reference band with the maximum at 1468 cm^{-1} (attributed to scissors vibrations of CH_2 group). The values of *OI* of the cups exploited during various periods of time are shown in Fig. 3. There is no time correlation of *OI* which can be understood if one takes into

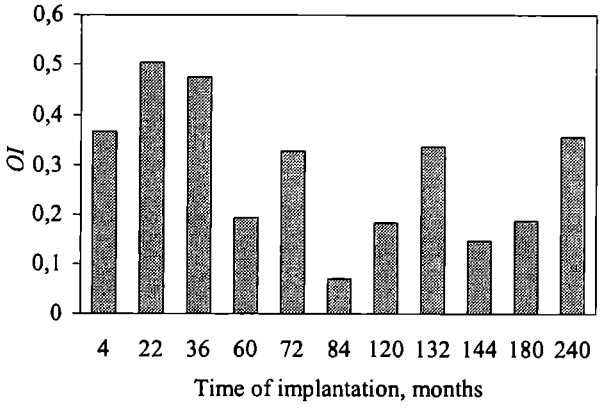

Fig. 3. Oxidation index (OI) of PE samples extracted from C_{AE} samples exploited various periods of time

account the fact that the deterioration of cups certainly depends on many factors including individual features of a patient, *e.g.* age, weight, physical mobility.

The IR analysis of C_{JJ} samples, carried out in the second step of our studies, showed that in this case the oxidation of PE is not detectable by means of FT-IR technique. The spectra of unused and exploited cups do not differ in the range of carbonyl absorption band. The reason of revising operations was mainly the loosening of the cups but not their cracking or breaking.

Hardness tests of the cups performed for both types of prostheses showed the decrease in hardness with the increasing exploitation time (see Fig. 4).

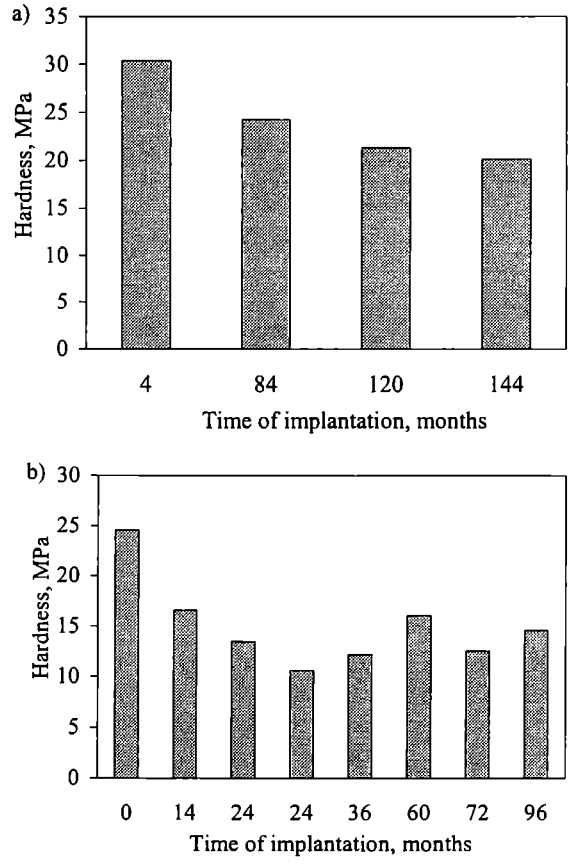

Fig. 4. The dependence of hardness on the time of implantation PE samples: a) C_{AE}, b) C_{JJ}

The viability of macrophages cultured with all the samples investigated was in the range 70—80%, which is a satisfactory result.

Therefore, it may be considered that the cause of premature wear off of polyethylene cups is the process of oxidation and accompanying polymer degradation. These processes may possibly be initiated during the production or sterilization of polyethylene bearings when primary polymer macroradicals may be formed and then react easily with oxygen. As a result of subsequent reactions with the participation of peroxy radi-

cals, peroxides and alkoxy radicals, oxidation of a polymer molecule occurs. This process, related to the break up of the main polymer chain and oxidative degradation, may also be the result of periprosthetic tissue reactions. Chemical degradation of the material may lower its mechanical resistance and accelerate the process of polyethylene cup wear off.

REFERENCES

1. Eyerer P.: *Biomed. Technik* 1983, **28**, 297.
2. Otfinowski J., Dudka J.: *Chir. Narz. Ruchu i Ortop. Pol.* 1991, **56**, 150.
3. Otfinowski J., Pawelec A.: *J. Bone Joint Surg.* 1995, **77-B**, 802.
4. Salvati E. A., Wright T. M., Burstein A. H., Jacobs B.: *J. Bone Joint Surg.* [*Am.*] 1979, **61-A**, 1239.
5. Thirupathi R. G., Husted C.: *Clin. Orthop.* 1983, **179**, 209.
6. Weightman B., Swanson S. V., Isaac G. H., Wróblewski B. M.: *J. Bone Joint Surg.* [*Br*] 1991, **73-B**, 806.
7. Chen J. H., Shih-Shyn Wu J.: *Comput. Methods Programs Biomed.* 2002, **68**, 117.
8. Dai X., Omori H., Okumura Y., Ando M., Oki H., Hashimoto N., Baba H.: *Artif. Organs* 2000, **24**, 746.
9. Maloney W. J., Galante J. O., Anderson M., Goldberg V., Harris W. H., Jacobs J., Kraay M., Lachiewicz P., Rubash H. E., Schulzer S., Woolson S. T.: *Clin. Orthop.* 1999, **369**, 157.
10. Devane P. A., Home J. G.: *Clin. Orthop.* 1999, **369**, 59.
11. Denizot R., Lang J.: *Immunol. Methods* 1986, **89**, 271.
12. Hummel, Scholl: "Atlas der Kunststoff — Analyse", vol. 1—2, Carl Hanser Verlag, München 1968, p. 124—126.