

MAREK SUDOŁ<sup>1)</sup>, KRYSZYNA CZAJA<sup>1)\*</sup>, JERZY CYBO<sup>2)</sup>, PIOTR DUDA<sup>2)</sup>

## Effect of electron-beam irradiation on structure of ultra high molecular weight polyethylene used in medical implants

### RAPID COMMUNICATION

**Summary** — Effect of electron beam irradiation with a dose equivalent to that used in practice during radiation sterilization of endoprostheses (26 kGy) or twice higher ( $2 \cdot 26$  kGy) on the change of UHMW-PE structure. UHMW-PE (trade name Chirulen 1120) is used for preparation of cups of hip endoprostheses. Structural changes of the polymer have been investigated using FT-IR method. Mainly the results of polymer oxidation (increase in the part of carbonyl groups of ketone, ester and perester types as well as of hydroxyl and vinyl groups) have been found. It was also found, using GPC method, that irradiation caused also partial degradation of macromolecules (reduction of molecular weight one order of magnitude) and crosslinking processes were favored by macroradicals formed (gel fraction part about 40 %, increase in melting temperature as well as in crystallinity degree) .

**Key words:** ultra high molecular weight polyethylene, endoprostheses, electron beam sterilization, oxidation, degradation, crosslinking, crystallinity.

Ultra high molecular weight polyethylene (UHMW-PE) has been widely used since the 1960s for the production of acetabular cups in total hip replacement [1—3]. This material is selected primarily due to the combination of properties such as high abrasion resistance, high toughness, low coefficient of friction, good chemical resistance and relatively low cost. An application of the polymer mentioned before requires its stability during the process of production and preparation to implantation and the resistance in the service conditions as well.

Prior to implantation within the body, UHMW-PE must be sterilized to prevent contamination. During the past 20 years the medical devices have been intensively sterilized by  $\gamma$ - or electron-beam irradiation and this trend is expected to be continued. However, while irradiation is a very clean, convenient and effective method for sterilization of implant materials, it also causes chemical and structural changes within the polymer matrix. When UHMW-PE exposed to irradiation, chemical bonds, such as carbon-hydrogen and carbon-carbon, are broken creating free radicals in the polymer chain. These radical are postulated to be involved in a variety of reac-

tions among which oxidative chains scission and crosslinking are identified as the two predominant ones [4—7]. The chemical changes alter the structure of UHMW-PE and lead to the changes in physical properties of this material.

It should be emphasized that physicochemical and mechanical properties of the material may also undergo significant changes in the long-term application due to the factors, such as X-ray examination, plastic deformation caused by patient's movement and the natural ageing of the polymer. It is suggested that the time-dependent changes are caused by the long-living free radicals found within the polymer matrix many years after irradiation [8]. Therefore it is considered that the cause of premature wear of polyethylene cup is the process of polymer oxidation as well as its degradation which are initiated by the long-living macroradicals [9].

Electron-beam irradiation of polymeric materials is a clean process which requires less energy and enables greater processing speed at room temperature in comparison with other processes what may limit undesirable oxidative reactions [10, 11]. Therefore this type of irradiation of different thermoplastics as well as rubbers have been extensively studied recently [10—16].

It is known that the type and magnitude of radiation-induced changes depend strongly on irradiation conditions (radiation source, absorbed dose, atmosphere) and the sample form. This paper describes the part of the

<sup>1)</sup> Opole University, Institute of Chemistry, ul. Oleska 48, 45-052 Opole, Poland.

<sup>2)</sup> University of Silesia, Faculty of Computer and Materials Sciences, ul. Śnieżna 2, 41-200 Sosnowiec, Poland.

<sup>\*)</sup> Author, to whom all correspondence should be addressed; e-mail: czaja@uni.opole.pl

study on the medical grade UHMW-PE, applied in the production of acetabular cups for hip replacement. In our previous papers [17, 18] the preliminary estimation of physicomaterial properties of the irradiated UHMW-PE was shown. Now investigation results of structure changes in this material, occurring upon sterilization with electron beam irradiation, are presented.

## EXPERIMENTAL

### Materials

Medical grade polyethylene used was Chirulen 1120 obtained from UHMW-PE powder synthesized in a low-pressure process in the presence of Ziegler catalysts (titanium, aluminum and chlorine content ranged from a few to 20 ppm as certified by the manufacturer, Poly Hi Solidur Deutschland GmbH). Since the powder shows extremely high melt viscosity — as a consequence of its very high molecular weight — it cannot be processed using the standard molding techniques. Therefore UHMW-PE powder was compression-molded into blocks from which the final surgical implants have been often produced by machining. The starting material for the study was semi-finished material in the form of a roller made of the polymer described above. Properties of UHMW-PE material used are presented in Table 1.

**Table 1.** Properties of Chirulen 1120 UHMW-PE type (molded forms)

Properties	Unit	Value
Density	kg/m <sup>3</sup>	973
Yield stress (23 °C)	MPa	23
Ultimate tensile strength (23 °C)	MPa	49.5
Elongation at break (23 °C)	%	512
Notched impact strength (23 °C)	kJ/m <sup>2</sup>	197

### Specimens preparation and sterilization

The test specimens were prepared as the slices of diameter  $\phi = 60$  mm and thickness of *ca.* 6 mm, cut from the roller. The initial sample A was not sterilized. Sample B was sterilized with electron-beam in the ambient environment and at dose of 26 kGy which is widely used dose in sterilization of PE medical materials. Sample C was irradiated with twice higher dose ( $2 \cdot 26$  kGy). This process was performed in the Institute of Nuclear Chemistry and Technology in Warsaw.

### FT-IR study

The polymer samples for FT-IR study are usually prepared as thin films by evaporating of the solvent from the polymer solution. However, such procedure was inapplicable for the polymer studied due to its low solubi-

lity in volatile solvents. We have not succeeded in preparation of the films by means of hot-molding in spite of applying various temperatures and pressures. It was found that such thermal treatment of the specimens causes the destructive changes in the polymer. Therefore the samples were prepared by cutting slips of a very smooth surface in order to ensure the sufficient transmission of IR radiation during the scans. In order to protect the material against overheating during the cutting, it was constantly cooled with demineralized water. The peripheral zones of these slips were discarded and the central part was divided into two equal fragments of the dimensions of 13x6x0.8 mm to give the objects for FT-IR study.

The spectra were recorded using Philips PU 9804 FT-IR spectrometer, at the constant spectral resolution of 2.0 cm<sup>-1</sup>. 20 scans of the sample sector were accumulated at the full range of wavenumber 4000—400 cm<sup>-1</sup>.

### GPC examination

Molecular weight and molecular weight distribution of the polymer were determined using high-temperature gel permeation chromatography (HT GPC). Waters 150-C apparatus fitted with one column with PL Gel 20  $\mu$ m Mixed-A packing manufactured by the Polymer Lab company was applied (the effective molecular weight  $M_w$  range was  $2 \cdot 10^3$ — $4 \cdot 10^7$ ). The samples were analyzed in 1,2,4-trichlorobenzene (TCB) solutions containing Sumilizer WX-R stabilizing agent, at 142 °C. The instrument was calibrated with polystyrene standards.

### DSC measurements

Melting point as well as relative crystallinity of the samples were measured using differential scanning calorimetry (DSC 2010 type Thermal Analysis System, TA Instruments). The heating rate was 10 °C/min in nitrogen. Heat of fusion ( $H_f$ ) was obtained by integrating of the area under endothermic peak. The degree of crystallinity of the sample was determined by assuming that the heat of fusion for the fully crystalline polyethylene was 290 J/g. Therefore, the degree of crystallinity ( $X$ ) was calculated by the equation of  $X = (H_f \text{ of sample} / 290) \times 100$ .

## RESULTS AND DISCUSSION

### Infrared spectroscopy

Infrared spectroscopy is one of the potentially suitable methods for studying the oxidative ageing of polymers. It was also applied by other authors for studying the UHMW-PE biomaterial [19—23]. In this paper FT-IR was applied in the analysis of the structural changes occurring in the polymer studied due to the external factors *i.e.* electron-beam irradiation.

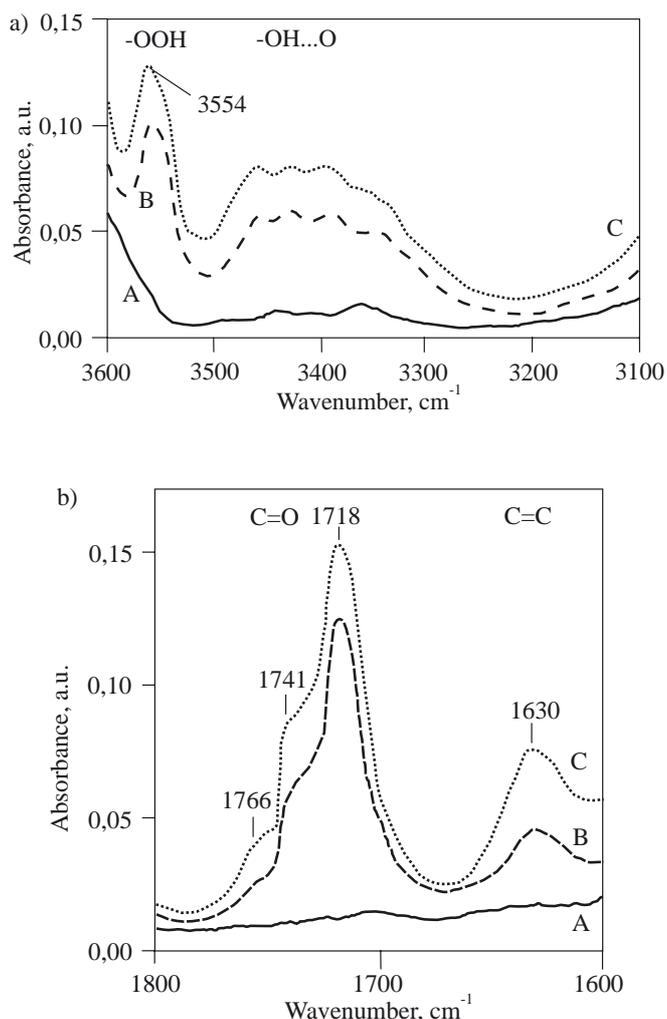


Fig. 1. FT-IR spectra of A, B and C samples in hydroxyl (a) and carbonyl (b) region

The series of analytical spectra of the samples studied in the hydroxyl and carbonyl range is shown in Fig. 1. The spectra of hydroxyl region ( $3100\text{--}3600\text{ cm}^{-1}$ ) recorded for the samples that underwent single electron-beam radiation sterilization (B) indicate the presence of oxidative polyethylene destruction and formation of hydroperoxide groups -OOH (the band at  $3554\text{ cm}^{-1}$ ) and different hydroxyl species -OH (the broad band in the range of  $3370\text{--}3515\text{ cm}^{-1}$ ). The similar phenomenon was also observed for the samples which were sterilized twice (C). The only difference is the higher content of hydroperoxides in the polymer matrix, in comparison with the samples which were sterilized once.

The analysis of the relevant bands in the carbonyl region ( $1600\text{--}1800\text{ cm}^{-1}$ ) confirms that electron-beam radiation causes the oxidative destruction of UHMW-PE. The spectra discussed contain the distinct carbonyl bands C=O of ketones  $R_1COR_2$  ( $1718\text{ cm}^{-1}$ ), as well as the less intense bands of esters  $O=C-O-C$  ( $1741\text{ cm}^{-1}$ ) and peresters  $O=C-O-O-C$  ( $1766\text{ cm}^{-1}$ ). The content of carbonyl groups increases clearly if the polymer samples are twice sterilized with electron-beam radiation.

Similar tendencies have been observed for the absorption bands characteristic for the unsaturated (vinyl) systems C=C ( $1630\text{ cm}^{-1}$ ). It should be stressed that the unsaturated systems, as the products of hydrocarbon dehydrogenation, are counted among the products of oxidation.

### Molecular weight and molecular weight distribution

The average results of GPC analysis indicate (Table 2) that molecular weight ( $\overline{M}_w$ ) of the polymer studied (sample A) is very high and the size of its molecules is diversified (molecular weight distribution  $MWD = 7.2$ ). We have also found that 30 % of the polymer did not dissolve in TCB, despite the long time of exposition to the solvent (up to 95 hours), which indicates that the polymer contains the fraction of a very high molecular weight of the order of a few million. Such long polymer chains prevent migration of the solvent molecules into the polymeric material which results in its partial insolubility. We attempted to increase the solubility *via* the prolonged contact with the solvent at the elevated temperature ( $150\text{ }^\circ\text{C}$ ). In these conditions the partial destruction of the polymer took place, which was indicated by the decrease in  $\overline{M}_w$ , especially for the shorter polymer chains ( $MWD$  increases).

Table 2. Effect of electron-beam irradiation on the properties of UHMW-PE

Sample	$M_w$	$MWD$	Residue insoluble in TCB at $142\text{ }^\circ\text{C}$ , %	Melting temp., $^\circ\text{C}$	Degree of crystallinity (X), %	
					whole sample	insoluble fraction
A	987 000	7.2	32	137.7	44	59
B	184 000	3.0	33	139.2	48	63
C	105 000	2.6	41	139.9	51	60

The results also indicate (Table 2) that the electron-beam irradiation causes polymer ageing processes. The molecular weight of the samples exposed to this radiation does not exceed  $2 \cdot 10^5\text{ g/mol}$  and their polydispersity is significantly lower ( $MWD = 2.5\text{--}3$ ). Hence, the average molecular weight decreases as the radiation dose is increased (*cf* A, B and C samples). It is concluded that the macromolecules undergo degradation which is caused by the electron-beam irradiation. This process affects mainly long chains, which is indicated by the significant decrease in the value of  $MWD$ .

It should be stressed that all the sterilized samples, as well as the polymer which was not exposed to radiation, did not dissolve in the conditions mentioned above. Therefore the results discussed refer to the soluble fraction of the polymer of lower molecular weight. The amount of insoluble residue (gel fraction) increases with

irradiation dose (Table 2). Therefore irradiation induces intermolecular recombination of radicals (crosslinking) and as a result the insoluble fraction containing the macromolecules of markedly higher molecular weight is obtained.

### DSC analysis

The average melting temperature and the degree of crystallinity determined by means of DSC for the polymers studied are shown in Table 2. The results obtained indicate that melting temperature of the polymer studied is relatively high, reaching 140 °C for irradiated samples, which confirms the fact that the molecular weight of this polymer is very high. The samples exposed to radiation tend to exhibit a slight increase in melting temperature and  $X$  value, which can be attributed to the increased crosslinking caused by the radicals formed in the process of irradiation.

As it was mentioned before, the study of molecular characteristics of the samples, especially those exposed to irradiation, was difficult due to their low solubility and impeded penetration of the solvent into the sample, which was probably caused by the process of crosslinking or the increase in the degree of crystallinity. To address this problem, we have carried out DSC analysis of the residues undissolved. The results obtained are also shown in Table 2. It should be emphasized that  $X$  value of insoluble residues is markedly higher and approximately constant (ca. 60 %), independently on the character of the initial sample.

### CONCLUSION

Electron-beam irradiation, in atmospheric air, of medical grade UHMW-PE leads to oxidation of the polymer. With the growing absorbed dose the concentration of carbonyl groups (ketones, esters and peresters) as well as hydroxyl and vinyl ones increases. The sterilization doses reduce the average molecular weight of the soluble fraction by approximately one order of magnitude (oxidative degradation) and cause the increase in the amount of insoluble (gel) fractions (crosslinking products). The irradiation tend to exhibit a slight increase in melting temperature and degree of crystallinity of the samples, which can be attributed to the increased cross-

linking caused by the radicals formed in the process of irradiation.

### REFERENCES

1. Jahan M. S., Wang C., Schwartz G., Davidson J. A.: *J. Biomed. Mater. Res.* 1991, **25**, 1005.
2. Buchanan F. J., White J. R., Sim B., Downes S.: *J. Mat. Sci.: Mater. Med.* 2001, **12**, 29.
3. Naheed N., Jahan M. S., Ridley M.: *Nucl. Instrum. Meth. B* 2003, **208**, 204.
4. Premnath V., Harris W. H., Jasty M., Merrill E. W.: *Biomaterials* 1996, **17**, 1741.
5. Hamilton J. V., Schmidt M. B., Greer K. W., Shah C.: *Radiat. Phys. Chem.* 1998, **52**, 283.
6. Singh A.: *Radiat. Phys. Chem.* 1999, **56**, 375.
7. Aydinli B., Tinçer T.: *Radiat. Phys. Chem.* 2001, **62**, 337.
8. O'Neill P., Birkinshaw C., Leahy J. J., Barklie R.: *Polym. Degrad. Stabil.* 1999, **63**, 31.
9. Kowal J., Czajkowska B., Żmihorska-Gotfryd A., Otfinowski J., Więcek A., Wierzbička A., Wojewoda J.: *Polimery* 2003, **48**, 537.
10. Żenkiewicz M.: *Polimery* 2003, **48**, 667.
11. Żenkiewicz M., Rauchfleisz M., Czupryńska J.: *Radiat. Phys. Chem.* 2003, **68**, 799.
12. Czupryńska J.: *Polimery* 2002, **47**, 8.
13. Liu I. -C., Tsiang R. C. -C.: *Nucl. Instr. Meth. B* 2002, **197**, 228.
14. Żenkiewicz M.: *Polimery* 2003, **48**, 66.
15. Żenkiewicz M., Rauchfleisz M., Czupryńska J.: *Polimery* 2003, **48**, 343.
16. Żenkiewicz M.: *Polimery* 2004, **49**, 94.
17. Duda P., Czaja K., Cybo J., Okrajni J., Myalski J.: *Chir. Narz. Ruchu Ortop. Pol.* 2001, **66**, 443.
18. Cybo J., Czaja K., Duda P., Sudoł M., Okrajni J.: *Chir. Narz. Ruchu Ortop. Pol.* 2002, **67**, 301.
19. Streicher R. M.: *Radiat. Phys. Chem.* 1995, **46**, 893.
20. Bruni P., Conti C., Corvi A., Rocchi M., Tosi G.: *Vibrational Spectroscopy* 2002, **29**, 103.
21. Aydinli B., Tinçer T.: *Radiat. Phys. Chem.* 2001, **62**, 337.
22. Hyun Kang P., Chang Nho Y.: *Radiat. Phys. Chem.* 2001, **60**, 79.
23. Taddei P., Affatato S., Fagnano C., Bordini B., Tinti A., Toni A.: *J. Mol. Struct.* 2002, **613**, 121.

Received 16 VIII 2004.