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Effect of electron beam irradiation and plastic deformation on molar mass of medical grade ultra-high molecular weight polyethylene

RAPID COMMUNICATION

Summary — Separated and combined electron beam irradiation (as a sterilization procedure) and plastic deformation effects on the average molar mass of ultra-high molecular weight polyethylene (UHMW-PE) were studied. It was found, that both irradiation and deformation have a different impact on the polymer structure. With the growing irradiation dose the mass-average molar mass ($\overline{M}_w$) of the polymer soluble fraction reduces and the amount of insoluble fraction (gel) increases. On the other hand, the plastic deformation of UHMW-PE alone may be considered as not involving any destruction of polymer macromolecules. The combined effect of these factors leads to different results in comparison to their separate action and depends on the sequence of the destructive impacts on the polymer. However independently of the sequence of both external factors their synergetic effect is observed for the degradation of UHMW-PE.

Key words: ultra-high molecular weight polyethylene, electron beam irradiation, plastic deformation, mass-average molar mass, polydispersity.

WPŁYW NAPROMIENIANIA STRUMIENIEM ELEKTRONÓW ORAZ DEFORMACJI PLASTYCZNEJ NA MASĘ MOLOWĄ POLIETYLENU ULTRAWIELKOCZĄSTECZKOWEGO DO ZASTOSOWAŃ MEDYCZNYCH

Streszczenie — Badano wpływ sterylizacji metodą napromieniania strumieniem elektronów oraz deformacji plastycznej (zgniatania, rys. 1) polietylenu ultrawielkocząsteczkowego (UHMW-PE), stosowanego do wytwarzania panewek endoprotez stawu biodrowego, na masę molową polimeru. Stwierdzono, że sterylizacja wpływa na utleniającą destrukcję makrocząsteczek polimeru, której stopień zależy od użytej dawki promieniowania (zmniejszenie masy molowej masowo średniej). Procesowi temu towarzyszy sieciowanie makrocząsteczek (wzrost udziału frakcji nierozpuszczalnej). Z kolei sama deformacja plastyczna wydaje się nie mieć wyraźnego wpływu na proces degradacji. Tymczasem łączne zastosowanie obydwu czynników zewnętrznych prowadzi do odmiennych efektów, dodatkowo zależnych od kolejności ich oddziaływania. W każdym wariancie oddziaływań zewnętrznych, w którym stosowana była sterylizacja radiacyjna strumieniem elektronów (niezależnie od kolejności stosowanych oddziaływań jak też w przypadku braku deformacji), następowała wyraźna destrukcja polimeru, prowadząca do zmniejszenia jego masy molowej z poziomu ok. 1000 kg/mol odpowiadającego próbce bazowej do wartości nie przekraczającej 200 kg/mol. Towarzyszące temu zmniejszenie polidyspersyjności z wartości ok. 10 do wartości 2—4 świadczy, że degradacji ulegały przede wszystkim nieusieciowane (rozpuszczalne) frakcje polimerowe o najdłuższych łańcuchach. Wyniki badań prowadzą także do wniosku, że odkształcenia plastyczne UHMW-PE zastosowane po jego sterylizacji radiacyjnej przyczyniają się w mniejszym stopniu do degradacji i sieciowania makrołańcuchów polimeru, niż w przypadku odwrotnej kolejności działania tych czynników. Jednak w obydwu przypadkach obserwuje się synergizm współdziałania obu czynników zewnętrznych na procesy destrukcyjne makrołańcuchów polietylenowych.

Słowa kluczowe: polietylen ultrawielkocząsteczkowy, napromienianie strumieniem elektronów, deformacja plastyczna, masa molowa masowo średnia, polidyspersyjność.

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Ultra-high molecular weight polyethylene (UHMW-PE) is applied in the production of surgical endoprostheses because of its favorable strength. This material is chosen primarily due to its combination of high abrasion resistance, high hardness, low coefficient of friction, low creep, good chemical resistance and relatively low cost. In contrast to these good properties, UHMW-PE in total joint replacement is most often observed due to wear which is considered to be the primary problem in orthopedic today [1—4]. Such an application of the polymer requires its stability during the process of orthopedic implants production, implantation and the resistance in the service conditions as well.

After fabrication UHMW-PE components for total joint replacement must be sterilized to prevent contamination. During the past 20 years the medical devices have been intensively sterilized by γ- and electron beam radiation and this trend is expected to continue. However, it is known that this sterilization process promotes oxidative chain scission and worsening desirable physical and mechanical properties of UHMW-PE [4]. Electron beam irradiation of polymers, as a cleaning process which requires less energy and enables a greater processing speed at room temperature in comparison with other processes, has been extensively studied recently [5—16].

A mechanical stress in the polymer has been also found to accelerate radiation-induced degradation. High cyclic stresses and oxidative degradation of the polymer are known to be primary contributing factors to an increased rate of wear [17, 18]. Meanwhile, the assembly of a metal part of an endoprosthesis in the cup of the polymer acetabulum requires very high compressing forces. Also, after an implant has been placed inside the patient's body, it is exposed to cyclic mechanical stresses [19]. Therefore the effect of plastic deformation on the properties of UHMW-PE has been the subject of many investigations [20—27].

In our previous study we studied the effect of electron beam irradiation on the structure of UHMW-PE used in medical implants [12]. It was found that irradiation reduces the average molar mass of the polymer soluble fraction by approximately one order of magnitude (oxidative degradation) and causes the increase of insoluble fractions (crosslinking process). The objective of this study was to determine the molecular changes (molar mass and molecular weight distribution) of the UHMW-PE as a result of separated and combined effects of electron beam irradiation and plastic deformation of the flat polymer profiles used in the production of hip-joint acetabular cups.

EXPERIMENTAL

Materials

The medical grade polyethylene used was Chirulen 1120 obtained from UHMW-PE powder synthesized in a low-pressure process in the presence of Ziegler catalysts (the titanium, aluminum and chlorine content ranged from a few ppm to 20 ppm as certified by the manufacturer, Poly Hi Solidur Deutschland GmbH which transforms this powder into bars). Since the powder has an extremely high melt viscosity — as a consequence of its very high molecular weight — it cannot be processed with the standard molding techniques. Therefore the UHMW-PE powder was compression-molded into blocks [yield stress (23 °C) 23 MPa, ultimate tensile strength (23 °C) 49.51 MPa, elongation at break (23 °C) 512 % and notched impact strength 197 kJ/m^2]. Final surgical implants are often produced by machining from these blocks.

Methods of testing

The object of the study was the semi-product from the process of preparation of Weller acetabulum endoprostheses in the form of a roller made from the polymer described above. The test specimens were prepared as slices of diameter $\phi = 60$ mm and thickness of *ca*. 6 mm, cut from this roller. They were exposed to squeezing forces enough to cause plastic deformation by 15, 30, 45 or 60 % (see Fig. 1) and/or electron beam sterilized at doses of either 26 kGy or 2 times 26 kGy (Grey) in the air. The specimens are characterized in Table 1.

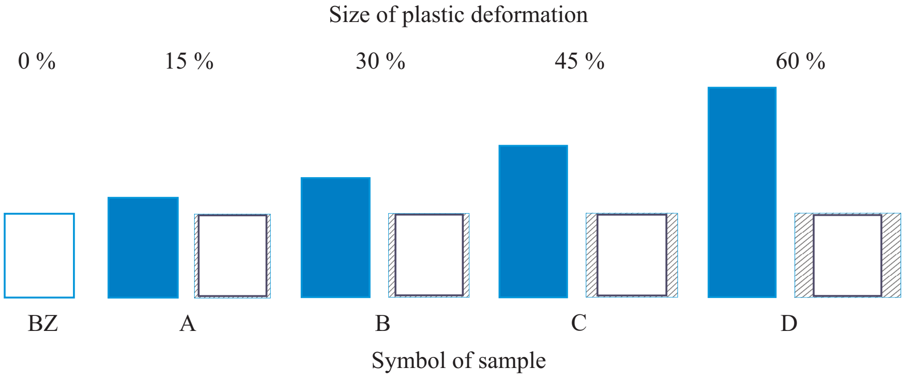

Fig. 1. Plastic deformation of UHMW-PE studied; grey — before and white — after sample squeezing (the shaded parts were removed)

T a b l e 1. Designation of samples subjected to electron beam irradiation and plastic deformation

Plastic defor-mation %		Irradiation after deformation		Deformation after irradiation	
	irradiation dose				
	0	1x26 kGy	2x26 kGy	1x26 kGy	2x26 kGy
0	BZ	1	2	—	—
15	A	A1	A2	1A	2A
30	B	B1	B2	1B	2B
45	C	C1	C2	1C	2C
60	D	D1	D2	—	—

The mass-average molar mass ($\overline{M}_w$) and molecular weight distribution of the polymer expressed by polydispersity ($PD = \overline{M}_w/\overline{M}_n$, where $\overline{M}_n$ denotes number-average molar mass) were determined using the high-temperature gel permeation chromatography (HT GPC). The Waters 150-C apparatus fitted with one column with the PL Gel 20 m Mixed-A packing manufactured by the Polymer Lab company was used (the effective molar mass range was 2—4000 kg/mol. The samples were analyzed as a 1,2,4-trichlorobenzene (TCB) solution containing the Sumilizer WX-R stabilizing agent. The polymer concentration ranged from 0.75 to 1.00 mg/cm^3. The analysis was carried out for two parallel samples of the same polymer solution. The instrument was calibrated with polystyrene standards.

RESULTS AND DISCUSSION

The average results of the GPC analysis presented in Table 2 (the BZ sample) indicate that $\overline{M}_w$ of the polymer studied is very high and the size of its molecules is diversified. We have also found that *ca.* 30 wt. % of the polymer sample did not dissolve in TCB, despite the long time of exposition to the solvent (up to 95 h), which indicates that the polymer contains a fraction of very high $\overline{M}_w$ of the order of a few thousand kg/mol. 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 through the prolonged contact with the solvent at the elevated temperature (150 °C). In these conditions polymer crosslinking processes for all versions of external impacts took place. Thus, the values of $\overline{M}_w$ and *PD* were found higher in analyses which followed version II (at 150 °C) than in analyses according to version I (at 142 °C), for nearly all analyzed samples. Increased temperatures from 142 °C up to 150 °C were responsible for molecular changes in the studied polymer probably as a result of crosslinking of macromolecules. Therefore the findings for molecular specifications from version I were considered more reliable.

Since there were no significant differences in $\overline{M}_w$ between the specimens after plastic deformation (A to D samples) and the initial polymer (BZ sample), the UHMW-PE plastic deformation processes may be considered as not causing any destruction of polymer macromolecules.

T a b l e 2. Results of molar mass ($\overline{M}_w$) and polydispersity (*PD*) determinations for samples dissolved under different conditions

Sample symbol	Conditions I (T = 142 °C/95 h)		Conditions II (T = 142 °C/48 h and T = 150 °C/48 h)		Residue insoluble in TCB wt. %
	$\overline{M}_w$, kg/mol	*PD*	$\overline{M}_w$, kg/mol	*PD*	
BZ	987	7.2	920	10.3	*ca.* 30
A	1278	14.3	991	15.3	20—30
B	962	10.9	881	10.9	
C	1336	10.6	934	20.1	
D	1244	8.6	1037	18.6	
1	184	3.0	198	5.4	*ca.* 35
A1	108	2.3	147	4.3	50—60
B1	165	2.6	158	5.8	
C1	119	2.6	164	3.6	
D1	138	2.6	157	3.7	
1A	136	2.5	246	7.0	30—50
1B	117	4.0	272	6.6	
1C	83	4.4	308	6.8	
2	105	2.6	122	4.2	*ca.* 40
A2	69	2.2	82	2.5	80—90
B2	64	2.1	75	2.7	
C2	56	2.1	72	3.0	
D2	75	2.3	76	3.0	
2A	100	3.1	121	2.8	60—80
2B	92	3.3	127	3.3	
2C	74	3.6	111	4.0	

After single irradiation of UHMW-PE samples, the $\overline{M}_w$ values of polymer is reduced as much as five times (from about 1 000 kg/mol down to about 200 kg/mol), and *PD* drops down more than twice (from 7.2 down to 3.0). The second irradiation of polyethylene with another dose of 26 kGy reduces further $\overline{M}_w$ but less than twice, only (from 184 kg/mol down to 105 kg/mol), and *PD* goes down from 3.0 to 2.6 only. Moreover, the irradiation causes the increase in TCB-insoluble fractions of the polymer by about 5 wt. % absolute per each sterilization dose (from 30 wt. % for BZ sample to 35 wt. % for sample 1, and to 40 wt. % for sample 2). That is most probably caused by the crosslinking process of short-chain fragments which yielded from degradation of polymer macromolecules — in particular from degradation of the longest ones (hence the drop in *PD*).

The analysis of molecular properties of the investigated samples leads to the conclusion that plastic deformations of UHMW-PE after its irradiation bring about less degradation of polymer macromolecules than when those factors are applied in the reverse order (Table 2). For the samples subjected to one or two irradiation doses after earlier plastic deformations (A1 to D1 samples) and (A2 to D2 samples), no clear relation is observed between the values of $\overline{M}_w$ weights, *PD* and the size of plastic deformation. On the other hand, for the UHMW-PE samples exposed to those factors in the reverse order (plastic deformation after single or double irradiation: 1A to 1C and 2A to 2C samples), diversification of data becomes clear. Thus, $\overline{M}_w$ of samples 1A to 1C and 2A to 2C declines for increasing plastic deformations, while *PD* increases in that case. That means easier degradation of polymer macromolecules by higher squeezing forces applied to UHMW-PE specimens, which have been earlier subjected to irradiation.

Moreover, attention should be paid to the fact that the synergic effect is observed for the destructive impact from both external factors, and it is observed both for the specimens subjected to plastic deformation and then to irradiation sterilization (samples A1 to D1 and A2 to D2), and for the specimens subjected to deformation after sterilization (1A to 1C and 2A to 2C samples).

The results obtained indicate that the electron beam irradiation causes polymer ageing processes. The $\overline{M}_w$ values of all the samples exposed to this radiation does not exceed 200 kg/mol and their polydispersity is significantly lower (*PD* = 2 to 4.5). The $\overline{M}_w$ decreases as the radiation dose is increased (*cf*. the BZ, 1 and 2 samples). It is concluded that the macromolecules undergo destruction, 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 *PD*. The decay of macromolecules induced by the electron beam irradiation is further enhanced if the sample was exposed to squeezing forces before. The results shown in Table 2 indicate that the $\overline{M}_w$ and *PD* are always lower for the samples exposed to both factors, comparing with the samples which were sterilized only. We have also observed that the synergic effect of both factors does not depend on the magnitude of the plastic deformation.

It should be also stressed that all the samples sterilized, as well as the polymer which was not exposed to radiation, did not dissolve in the conditions mentioned above. The amount of insoluble residue (gel fraction) was markedly higher for the samples which were exposed to radiation (Table 2) and it was even higher for the samples exposed to both factors. Therefore the results discussed above refer to the soluble fraction of the polymer of lower molar mass. A considerable amount of polymer sample, which reached even 90 wt. % in the extreme case, failed to dissolve.

CONCLUSIONS

Our results of the molecular weight study prove that every type of external impact, like plastic deformation of UHMW-PE and/or its irradiation with the electron beam, has the modifying effect on the structure of the polymer. The action of those destructive factors on the tested material, individually or collectively, *i.e.* one after another, yields different final results. The irradiation leads to degradation of macromolecules and this process affects mainly long chains, which is indicated by the significant decrease in the value of *PD* (the share of soluble fraction is nearly the same). On the other hand, the plastic deformation of UHMW-PE may be considered as not involving any destruction of polymer macrochains. Meanwhile, the combined effect of these factors leads to different results, compared to the separate action. A mechanical stress in the polymer was found to accelerate radiation-induced degradation. The analysis of molecular properties of the investigated samples leads to the conclusion that the degradation of the macromolecules depends on the sequence of the destructive impacts on the polymer. The plastic deformation of UHMW-PE used after its irradiation brings about less degradation of polymer than when those factors are applied in the reverse order. Additionally, independently of the sequence of both external factors, their synergic effect is observed for the destructive impacts of UHMW-PE.

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