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THE ANALYSIS OF CHANGES OF THERMAL PROPERTIES AND STRUCTURES OF THE BONE CEMENTS AFTER AGEING PROCESSES

Abstract. This paper presents the results of the investigations of thermal properties and the structure of bone cements developed based on polymethyl methacrylate with addition of fillers and auxiliaries. DSC method was employed to determine glass transition temperature for the studied bone cements before and after the process of aging in water NaCl solution subject to electrolysis. The investigations were carried out for bone cements with different composition and different percentage share of the components. Two types of bone cements were used for the investigations: CMW1 manufactured by CMW and Palamed 40. Thermal properties were analysed using differential scanning calorimetry by means of Netzsch DSC 200 Phox equipment. The structure was examined by means of Nikon Eclipse E 200 optical microscope.

1. INTRODUCTION

Bone cements based on polymethyl methacrylate were used in orthopaedics worldwide as early as in the fifties of the 20th century [1]. A range of their biomechanical advantages which could be obtained through cementing prostheses has made them a natural binding material for joint implants [1-4].

Polymer component (powder) for bone cement is polymethyl methacrylate (PMMA), which is a product of polymerization of methyl methacrylate (a thermoplastic). In some cases it is a copolymer of methyl methacrylate (MMA) and styrene (Simplex – P) or methyl acrylate (Palacos) [5]. Polymer in the form of powder is a product of suspension polymerization or a mechanically grinded product of block polymerization. The powder in this compound is in the form of regular spheres or irregular particles with more developed surface and diameters ranging from a fraction to several hundreds of micrometers, predominantly being 5 – 90 µm. An integral part of powder component is an initiator of polymerization process, benzoyl peroxide with the amount ranging from 0.5% (Palacos) to 3% (CMW) and sometimes contrast medium for radiological examinations in the form of barium sulphate (AKZ, Acrybond, CMW) or zirconium dioxide (Palacos R, Simplex – RO, Implast) added with the amount of up to 15%. A liquid monomer component is usually MMA, sometimes its mixture with other acryl monomers, i.e. butyl methacrylate (Sulfix – 6). Both components of bone cement i.e. powder and fluid, are mixed with weight ratio of from 1.7:1 to 3:1, depending on the resultant commercial product. The components are prepared by producers in the required proportions and in suitable packages [5]. Acryl bone cements are polymerized after mixing of both components according to radical mechanism. An initiator of polymerization is benzoyl peroxide from powder component. Activation energy for creation of free radicals of benzoyl peroxide is reduced as a result of using a catalyst (DMPD) from liquid component. Using of this type of redox system (oxidation – reduction) allows for polymerization reaction which occurs very fast (several minutes) even in room temperature [6-10]. Macroscopically polymerized mass is composed of aggregates of polymer with dimensions of 10-18 micrometers connected with the bridges of polymerized monomer. During polymerization, this material is plastic and can be formed easily while it penetrates even deep into the fine trabecular structures in bone. Polymer is solidified in less than 10 minutes from the beginning of mixing (powder + fluid), which is a time required for fixation of prostheses [5]. Many physical and chemical processes occur during formation of bone cement, as a result of which a structure of mutually combined PMMA and PMMA chains is obtained in situ [11].

Working environments for cements are very aggressive, which considerably elevates the aging rate and causes intensified chipping of cement, which results in weakening of bone-cement-implant system. This phenomenon might lead to loosening of prosthesis and the necessity to perform implantation. Another negative effect of ageing and cement chipping is the phenomenon of emission of cement particles to human body. These particles, moving inside the body are deposited in different organs, e.g. liver, kidney etc. causing pathologies [5].

The study presents the results of investigations of thermal properties and the structures of bone cements manufactured from polymethyl methacrylate (PMMA) with addition of fillers and auxiliary media. The investigations were carried out for bone cements from different manufacturers, with different composition and percentage of components. Depending on physical state of polymer materials and the environments they work in, different uncontrolled phenomena might occur, including degradation, depolymerisation, destruction and residual processes of polymerization, cross-linking, hydrolysis. These phenomena lead to aging process, which causes irrecoverable adverse changes in the materials. The term aging is used for determination of changes in physical properties of polymers caused by chemical, thermal, biological, mechanical or photochemical reactions which cause breaking of macromolecule chain [12, 13]. In order to learn more about the effect of the process of aging on a particular polymer material, one should carry out aging examinations under working condition. However, the duration of the process causes that the methods of accelerated aging are employed, at which high frequency of effect of agents on polymer material causes acceleration of the process.

DSC method allowed for determination of vitrification temperature in the studied bone cements before and after the process of aging in water solution of NaCl subjected to electrolysis. Differential scanning calorimetry (DSC) is a method used for examination of thermal effects which occur in particular time under isothermal conditions. Measurement of heat which is generated as a result of chemical reactions and physical processes is taken directly. DSC allows for obtaining of information about thermodynamic reactions in a particular process. Knowledge of the course of the process allows for determination of the relationships between molecular parameters and properties of polymer materials [14, 15].

2. MATERIAL AND METHODOLOGY

Materials used for the investigations were bone cements: CMW1 manufactured by CMW Laboratories Dentsply and Palamed 40 manufactured by Heraeus Kulzer GmbH.

Samples with dimensions of 50x10x4 mm were obtained at the temperature of 21 °C from the components delivered by the manufacturer according to the following procedure:

- chemical components in the form of fluid were poured to a sterile container,
- the container was filled with chemical components in the form of powder while evenly distributing it in the fluid,
- mixing of components was made with mixing time of 60 s,

- after mixing stage was completed, the mixture was left for 3 minutes required for viscosity to be sufficient,
- application tool was used to put the mixture to the mould,
- the process of polymerization was completed after 7 minutes from application of the material to the mould and then the samples were removed,
- the examinations were carried out 24 hours after polymerization.

Ageing was conducted in water solution of NaCl with concentration of 25% and pH 8, where the samples were placed. The process of electrolysis was carried out with the following parameters:

- direct current with intensity of 0.3A, voltage 4.3V, duration 720h.

DSC examination of bone cements were carried out using scanning microcalorymeter Netzsch PC-200. DSC curves were recorded during heating of samples at the rate of 10 ºC/min within the range of temperatures from 20 to 200 °C. Preparations for DSC examination were cut out from the samples obtained during polymerization of components of bone cements. PC 200 Netzsch apparatus software was employed for determination of glass transition temperature. The software allowed for examination of thermogravimetric curves within the set range of temperature. The model material was indium and sample mass was from 8 to 12 mg. The samples were weighted by means of SARTORIUS balance with accuracy of 0.01 mg, with external calibration and closed measurement chamber. The examinations were carried out according to current standards.

Structure examinations were carried out using optical microscope Nikon Eclipse E 200. The samples with thickness of 16-22 µm were used for investigations, cut out from sample core by means of microtome manufactured by Thermo Electron Corporation.

3. RESULTS AND ANALYSIS

Results of DSC examinations obtained from computations by means of Netzch software are compared in Table 1.

Table 1. The results of DSC investigations obtained from calculations of the Netzch programme

Samples	Glass transition temperature - PMMA, ºC
CMW1	109,7
CMW1 after ageing	104,3
Palamed 40	108,3
Palamed 40 after ageing	102,4

Figure 1 present DSC thermograms for bone cements in the study before and after the process of aging. Analysis of thermograms for the bone cements reveals that the shape of curves varies. This concerns in particular the changes in the value of glass transition temperature depending on chemical constitution of bone cements and aging process.

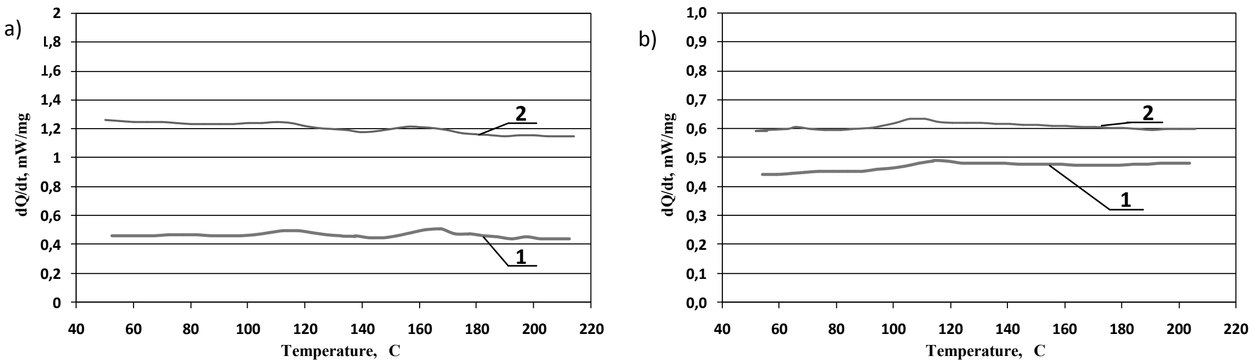

Fig. 1. Thermograms DSC of the: a) CMW1 bone cement, b) Palamed 40 bone cement; 1 - before ageing , 2 - after ageing

Value of energy absorbed by polymer material during aging of the samples rose both in the case of CMW1 and Palamed 40. In the area of temperatures lower than glass transition temperature, polymer material remains hard and brittle. In the vitreous zone, thermal energy is insufficient to overcome potential barrier for transfer and rotational movements of particle segments. The system remains in the state of thermodynamic non-equilibrium. In the zone of vitreous transition Brownian motion is initiated in molecular chain. Thermal energy becomes comparable to the barrier of potential energy to chain rotation. Glass transition temperature depends on chemical and molecular structures of bone cements depending on the types and the amount of used components. Lower values of glass transition temperature registered during investigations by means of DSC method for samples made of bone cements after the process of aging confirm the change in properties and structure of the materials used for the study. Glass transition temperature is closely connected with mobility of macroparticles which is affected by coherence of the structure and free volume [16].

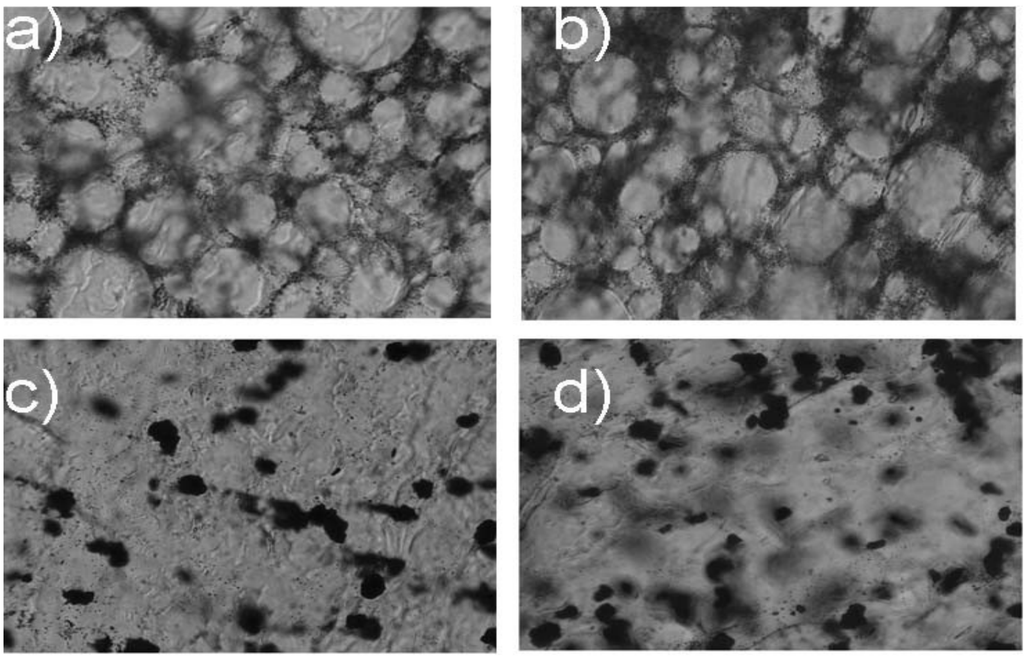

Fig. 2. Structure observed on optical microscope with magnification of 200x: a) CMW1 bone cement before ageing, b) CMW1 bone cement after ageing, c) Palamed 40 bone cement before ageing, d) Palamed 40 bone cement after ageing

Increase in glass transition temperature occurs with an increase in concentration of components contained in the composite [15]. Lower mobility of chains can be observed in this case and it results in higher glass transition temperature compared to bone cement before aging. Lower values of glass transition temperature after aging confirm occurrence of free volumes in the structure of bone cements in the study (Fig. 2b, d) as a result of material degradation.

4. SUMMARY

Properties shown by bone cement which is a binding material for connecting prosthesis with bone have considerable effect on durability and biofunctionality of artificial hip joint.

Bone cement used during hip joint replacement should be characterized by high biocompatibility, biotolerance and resistance to degradation and emission of particles to human body. Specific working environment for artificial hip joint, which is chemically aggressive, forces the necessity to ensure the resistance to aging, since the process leads to degradation of polymer material, causes chipping of the material and weakens the system of bone-cement implant.

Properties of studied bone cements depend considerably on the content of fillers and auxiliary media. Analysis of DSC thermograms reveals changes in the value of vitrification temperature for PMMA after the process of aging of the materials in water solution of NaCl subjected to electrolysis. Lower values of glass transition temperature were obtained for the samples made of bone cements after the process of ageing. The scope of changes in the analysed properties is similar for the bone cements in the study.

ACKNOWLEDGMENTS
This work was supported by the Foundation for Polish Science – TEAM project 2010-2014.

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ANALIZA ZMIAN WŁAŚCIWOŚCI TERMICZNYCH I STRUKTURY CEMENTU KOSTNEGO PO PROCESACH STARZENIA

Streszczenie: W artykule określono metodą DSC wartości temperatury zeszklenia PMMA przed i po procesie starzenia w roztworze wodnym NaCl poddanym elektrolizie. Badania przeprowadzono dla PMMA o różnym składzie i udziale procentowym składników. Do badań zastosowano dwa rodzaje cementów kostnych: CMW1 oraz Palamed 40. Dla części materiału badawczego przeprowadzono proces przyspieszonego starzenia w celu określenia odporności chemicznej na czynniki powodujące korozję i degradację cementu kostnego. Badania właściwości termicznych wykonano metodą różnicowej kalorymetrii skaningowej, wykorzystując urządzenie DSC 200 Phox firmy Netzsch. Strukturę obserwowano pod mikroskopem optycznym firmy Nikon Eclipse E 200.