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Original paper

# Time and mixing technique-dependent changes in bone cement SmartSet® HV

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For the past fifty years bone cements based on polymethylmethacrylate (PMMA) have been used in orthopaedic surgery for fixation of endoprostheses, especially in the cases of total hip replacement. It was shown that during this period vacuum mixing minimalizes the number of unwanted pores and thereby influences the mechanical properties of the cement. It was also discovered that later polymerization of the cement after its implantation lasts up to 6 months and changes its mechanical properties. In this study, mechanical properties (microhardness and elastic modulus measured by microindentation) of hand- and vacuum-mixed acrylic bone cement SmartSet HV® were investigated and compared after different time of cement exposition. This study points out that the measures of changes occurring with time in mechanical properties of differently mixed cement samples are equal but microhardness and elastic modulus are different and depend upon the technology of mixing.

*Key words*: *bone cement, microhardness, elastic modulus, ageing*

## 1. Introduction

Since bone cements of different composition have been used in orthopaedic surgery with good clinical results as bone filling agents in repairing procedure or for implant fixation in total hip replacement, a large number of papers have been published on their use. Most of these papers deal with the biocompatibility and thermal characteristics of cements but a little attention is devoted to possible changes of their mechanical properties dependent on mixing technique, which can occur with the time. Because of this reason the influence of mixing technique on some mechanical properties of acrylic bone cement SmartSet® HV was investigated in this study.

Most of commercially available acrylic bone cements are based upon polymethylmethacrylate (PMMA) and metylmethacrylate (MMA) systems and consist of powdered and liquid components [1], [2]. After mixing the compounds together, the exothermal radical polymerization of the monomer (included in liquid) begins. During this process free radicals break the covalent double bonds between the carbons of the monomer allowing them to bind to the lengthening polymer chains, and the pre-polymerized PMMA beads (included in powder) are gradually covered with the polymerizing monomer. The local amount of heat generated by the chemical reactions during the polymerization process depends on the thickness of the cement mantle, e.g., on the amount of polymerizing monomer [3], [4]. Properly cleaned and prepared bone canal is then filled with polymerizing bone cement and the endoprosthesis is inserted into the mass which within several minutes forms into solid cement mantle. The hardened cements have much lower modulus of elasticity than the metal endoprosthesis, but they are stiff enough and fully biocompatible. Their primary function is to provide a stable interface between the prosthetic implant and the surrounding bone and

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load distribution from the implant to the surrounding tissues [4].

Chemical composition and microstructure have the greatest influence on the mechanical behaviour of bone cement. The molecular weight of the interstitial matrix polymer for bone cements usually differs from the pre-polymerized PMMA beads, thus the matrix and interface between the matrix and the beads will determine the mechanical and time-dependent properties [5].

Because no studies have been published on the ageing of bone cement SmartSet® HV, the theoretical presumptions of the results of this research must come out from the previous studies based on other types of bone cements. In a research devoted to time-dependent changes in mechanical properties of bone cement Simplex® P, GOMOLL et al. [6] investigated the yield strength and elastic modulus of this cement 4 weeks after sample preparation and storage in a mixture of 90% Ringer's and 10% bovine serum at 37 ºC in darkness. The elastic modulus increased significantly two days after mixing, thereafter it dropped in additional 4 weeks. The average yield strength also demonstrated a strong time-dependence with an initial low value at two hours followed by a significant increase to a maximum after 2 weeks and smooth drop after next 2 weeks. Another study finding out the time problem of ageing conditions by BALEANI et al. [7] showed that the ageing conditions of the mechanically tested samples affected the results as well. LOONEY et al. [8] investigated the changes in mechanical properties and free radical concentration (which is connected with the stage of curing process) of Simplex® P bone cement in vivo and also under in vitro conditions. The measurements showed that the curing (disappearance of free radicals) of in vivo samples took a much longer time (more than 4 weeks) than in vitro curing (less than 2 weeks). The mechanical tests indicated that irrespective of ageing the cement in vivo or in vitro, its strength increased rapidly for the first 2 weeks and then its slight increase was observed for up to 6 months.

After acquaintance with the results of these or some other studies devoted to mechanical properties of bone cements after ageing, one perhaps recognizes that the "time question" represents a significant problem in bone cement research which can be solved only by standardization of sample storage conditions and time periods between mixing and sample testing dates. This solution might eliminate the differences between the results of several studies aimed at the properties of various bone cements and might give more accurate prediction of their long-time behaviour in vivo.

# 2. Material and methods

As an experimental material for this study a SmartSet® HV acrylic bone cement was used. Its quantitative composition is given in table 1.

Table 1. Quantitative composition of bone cement SmartSet® HV (%w/w)

| Bone cement powder | | | Bone cement liquid | | |
|---|---|---|---|---|---|
| MMA/MA copolymer | di-benzoyl peroxide | zirconium dioxide | MMA | *n*,*n*-dimethyl-*p*-toluidine | hydroquinone |
| 84 | 1 | 15 | 97.5 | ≤ 2.5 | 0.0075 |

A colourless and flammable liquid component emitts a distinctive odour. Its major component is the methylmethacrylate (MMA) monomer. Hydroquinone is a stabilizer preventing premature polymerization which may occur when the liquid is exposed to heat or light. *N*,*n*-dimethyl-*p*-toluidine is added to promote cement polymerization following the mixing of the powder and liquid components. The powdered component is a white and fine dust composed of a polymethylmethacrylate (PMMA)-based polymer. Dibenzoyl peroxide initiates cement polymerization when the powder and liquid components are mixed. This component contains also the radiopaque agent, zirconium dioxide.

For comparison, two mixing methods (hand and vacuum mixing) of the cement were used, both with exact timing as manufacturer recommends. Hand mixing was performed in a suitable, clean, dry mixing ceramic bowl when the liquid component was added into cement powder. The dough was mixed carefully to minimize the air entrapment, then it was taken into hands and kneaded for a few seconds. For vacuum mixing a CEMVAC™ mixing system was used at a mean pressure of 92.65 ±30.7 kPa [9]. The viscous dough was then poured into metal mould where the cement was hardened for about 15 minutes. The samples obtained after hardening process, 4 mm × 4 mm × 50 mm, were stored in air at 22 ±2 °C for different periods.

On the device MicroCombi Tester (MCT) microhardness and elastic modulus were determined by indentation measurements. In the instrumented indentation test, an indenter, i.e. a diamond pyramid (Vickers), was pressed vertically into the surface of the samples. During the test procedure the load $F$ and the indentation depth $h$ were measured during loading and also unloading. The result of the test procedure is the correlation between test load $F$ and the corresponding indentation depth $h$. The start of the test was defined as the moment of contact between the indenter and the surface of the sample. The indentation depth $h$ measured under test load includes the elastic and the plastic deformations.

The **indentation hardness** $H_{IT}$ was calculated from the test force $F$ divided by the projected area of the indenter in contact with the test piece ($A(h_c)$) at maximum load:

$$H_{IT} = \frac{F_{max}}{A(h_c)}.$$

The projected contact area $A(h_c)$ was calculated based on the knowledge of the geometry of the indenter and the stiffness of the contact.

The **indentation modulus** $E_{IT}$ was calculated from the slope of the unloading curve:

$$E_{IT} = \frac{1-\upsilon_{IT}^2}{\frac{2\cdot\sqrt{A(h_c)}}{\pi\cdot S} - \frac{1-\upsilon_i^2}{E_i}},$$

where $\upsilon_{IT}$ and $\upsilon_i$ are the respective values of Poisson's ratio of the test piece and of the indenter, $S$ is the slope of the tangent of the force/indentation curve during the unloading cycle, $h_c$ is the contact depth value dependent on the shape of the indenter, and $E_i$ is the elastic modulus of the indenter used. For homogeneous and isotropic materials $E_{IT}$ approaches the Young's modulus [10].

Our further investigation was focused on *planar porosity* of the bone cement tested. It was evaluated based on 20 random cuts for each mixing technique using light microscope Carl Zeiss SteREO Discovery V8 and appropriate software Axio Imager.

# 3. Results

The indentation tests were performed 20 times on each type of bone cement samples prepared by hand- and vacuum-mixing techniques after different storage periods. The list of samples and further used abbreviations can be found in table 2.

Table 2. List of samples and the abbreviations used

| Mixing technique | Age of samples | Abbreviation |
|---|---|---|
| Hand | 16 weeks | H 16 |
| | 2 weeks | H 2 |
| Vacuum | 24 weeks | CEMVAC 24 |
| | 2 weeks | CEMVAC 2 |

In all measurements, the Vickers diamond indenter with 200 μm diagonal was used. The curves representing loading and unloading were linear with 10 N/min slope and with pause at maximal force for 5 seconds. The measured force vs. penetration depth curves are plotted in figures 1–4 and the calculated values of $H_{IT}$ and $E_{IT}$ by the method of Oliver & Pharr are listed in table 3.

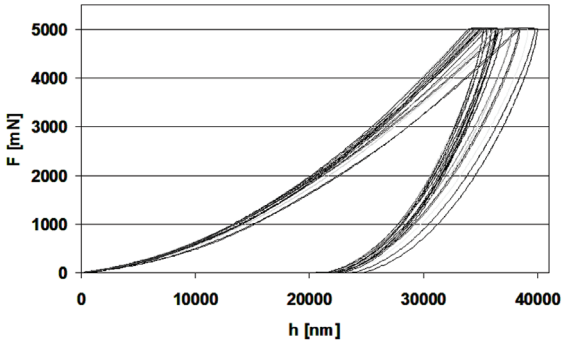


Fig. 1. Indentation curves for samples H16

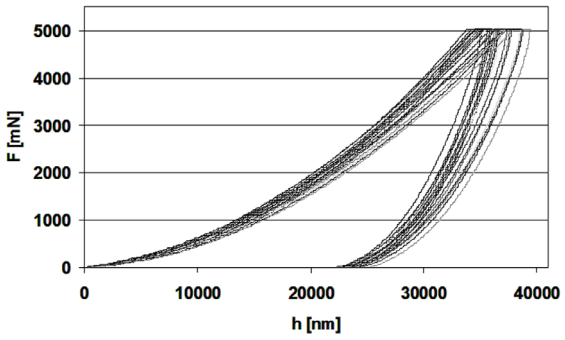


Fig. 2. Indentation curves for samples H2

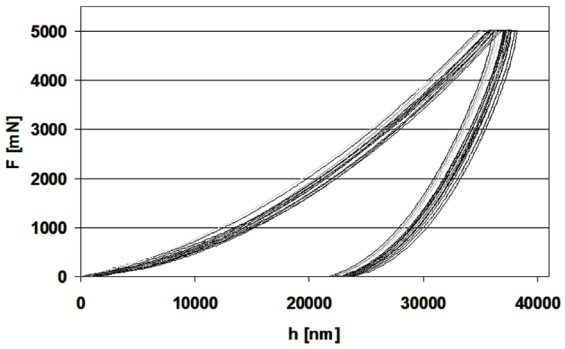


Fig. 3. Indentation curves for samples CEMVAC 24

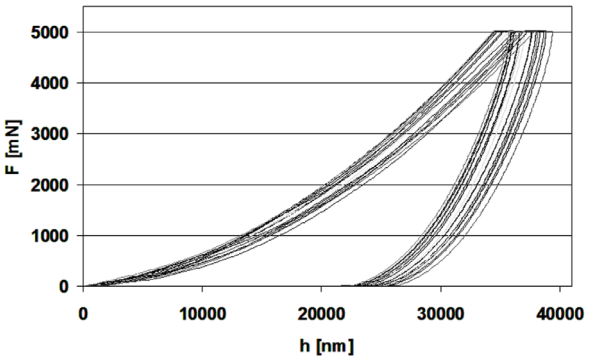


Fig. 4. Indentation curves for samples CEMVAC 2

by planar porosity measurements. The measured values of microhardness and elastic modulus of vacuum-mixed samples have lower standard deviations than the hand-mixed ones resting in technology of mixing under reduced pressure in the CEMVAC™ mixing system.

When comparing the indentation hardness of samples exposed for the same period but prepared by different techniques (H2, CEMVAC 2), it can be recognized that the samples mixed under vacuum have lower indentation hardness but higher indentation modulus than the samples mixed in the air.

Table 3. Calculated values of indentation hardness $H_{IT}$ and indentation modulus $E_{IT}$

| $n = 20$ | H 16 | H 2 | CEMVAC 24 | CEMVAC 2 |
|---|---|---|---|---|
| $H_{IT}$ (MPa) | 207.176 ± 2.952 | 199.087 ± 2.702 | 205.012 ± 1.789 | 193.473 ± 2.835 |
| $E_{IT}$ (Gpa) | 3.388 ± 0.096 | 3.687 ± 0.085 | 3.347 ± 0.021 | 3.789 ± 0.037 |

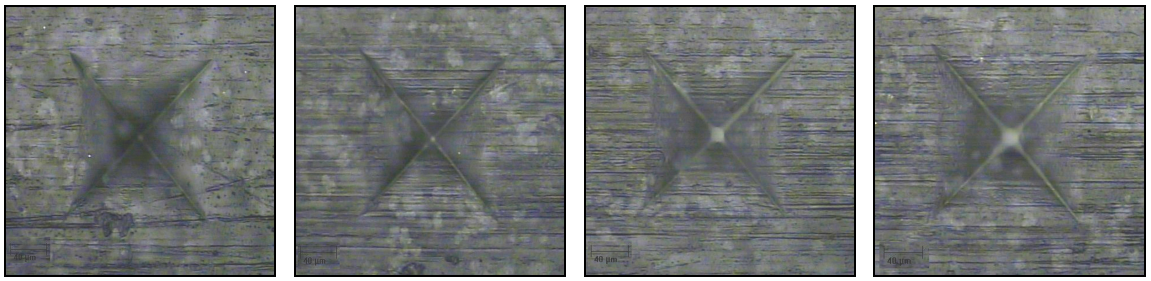

Fig. 5. Impressions after indentation tests and the structure of surface of bone cement SmartSet® HV

After indentation tests a planar porosity was evaluated which presents 4.43% for hand-mixed samples and 1.91% for samples mixed with the CEMVAC™ system.

# 4. Discussion

This paper presents a preliminary study of microhardness and elastic modulus of bone cement SmartSet® HV used in a today orthopaedic surgery. The variation in properties within each set of samples indicates that all of the cement matrices may have large local variations in microporosity which influences their mechanical properties the most [11]. Because the microhardness is related to matrix density, the density of each matrix was not constant but changed from one location to another.

From the results of indentation measurements it can be clearly seen that the structure of hand-mixed samples is largely inhomogeneous due to larger amount of pores in the matrices which has been proved

The dependence of measured mechanical properties of the tested bone cement on the time of exposition is also evident, whilst a significant increase of the indentation hardness with time occurred for hand-mixed samples and for vacuum-mixed samples. On the other hand, the elastic modulus of the samples has decreased for both techniques of mixing. Different viscoelastic behaviour of the bone cement tested caused by mixing technology and ageing on the air was also observed in our other measurements which testify to the changes in the cement matrix but have not been published yet. The results of indentation measurements correspond to the results reported by GOMOLL et al. [5]. Changes in the values of microhardness occurring with time can be explained by later polymerization of the cement mass (i.e. of the stranded monomer in the matrix) which may last up to next 6 months after its curing period [7]. In order to confirm this theory, an analysis of structure and substructure and investigation of the dependence of molar mass and its distribution on exposition time and manufacturing technology are desirable for the tested type of cement.

One can notice that changes in the tested properties of hand- and vacuum-mixed samples cannot be compared because of different time of their exposition. By converting the changes occurring in $H_{IT}$ and $E_{IT}$ to equal time unit (e.g., week) this objection can be overcome. After converting it is clear that the measures of changes in $H_{IT}$ and $E_{IT}$ are equal for both techniques of mixing, but the dynamics of changes still cannot be specified. For an exact estimation of the dynamics of property changes it would be necessary to carry out more measurements during the selected testing period.

Anyway, this study points out that mechanical properties of bone cement SmartSet® HV stored in the air are gradually changing with the time. As the other commercial bone cements based on acrylates have very similar chemical composition, also similar changes in their mechanical properties are expected. This fact can partially explain the differences between the results of several studies being aimed at the mechanical properties of various bone cements and published all over the world in spite of equal measurement conditions. Our results corresponding to other findings [6], [7], [8] clearly demonstrate the need for standardizing the storage parameters of acrylic bone cements before their testing.

# 5. Conclusions

- The variation in properties within each set of samples indicates that the structure of all of the samples is locally inhomogeneous which is caused by micro- and macropores.
- Larger amount of pores in the samples was observed for hand-mixed ones.
- The indentation hardness increases and the elastic modulus decreases simultaneously with the time of exposition for both techniques of mixing.
- The measure of changes in $H_{IT}$ and $E_{IT}$ was not caused by the technique of mixing.
- The paradox of the $H_{IT}$ and $E_{IT}$ dependence measured by this method should have been caused by different measure of creep connected with plastic deformation and followed by constant loading.
- The results corresponding to other findings clearly demonstrate the need for a standardization of storage parameters of acrylic bone cements before testing.

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