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MICROINDENTATION OF POLYMETHYL METHACRYLATE (PMMA) BASED BONE CEMENT

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Abstract: *Characterization of polymethyl methacrylate (PMMA) based bone cement subjected to cyclical loading using microindentation technique is presented in this paper. Indentation technique represents flexible mechanical testing due to its simplicity, minimal specimen preparation and short time needed for tests. The mechanical response of bone cement samples was studied. Realised microindentation enabled determination of the indentation testing hardness HIT and indentation modulus EIT of the observed bone cement. Analysis of optical photographs of the imprints showed that this technique can be effectively used for characterization of bone cements.*
Keywords: *Biomaterials, Polymethyl methacrylate (PMMA), Bone cement, Microindentation*

1. INTRODUCTION

Polymers are large molecules synthesized from smaller molecules, called monomers. Polymers for medical applications can be divided into three general fields:

1. Polymers for artificial joints
2. Bioabsorbable polymers for surgical applications
3. Adhesives for medical applications

An acrylate polymers, commonly known as acrylics or polyacrylates, belongs to a group of polymers which could be referred to generally as plastics. They are noted for their transparency and resistance to breakage and elasticity. Polyacrylates are based on acrylic acid, methacrylic acid, and their esters. Among them, polymethyl methacrylate (PMMA) is largely used for biomedical applications. The clinical history of polyacrylates began when it was unexpectedly discovered that the fragments of PMMA plastic aircraft canopies stayed in the body of the wounded without any adverse chronic reactions [1]. PMMA has been used as self-polymerising bone cement in orthopaedics since the 1960s. Acrylic bone cement is used to fill the irregular space between prosthesis and bone during total hip replacements in order to keep the prosthesis in place (Fig. 1). The primary functions of bone cement, when used to anchor artificial joints, are to secure the orthopedic implants to bone and transfer mechanical loads from the implant to the bone. Approximately 50% of all orthopedic implants utilize bone cement to achieve implant fixation [2].

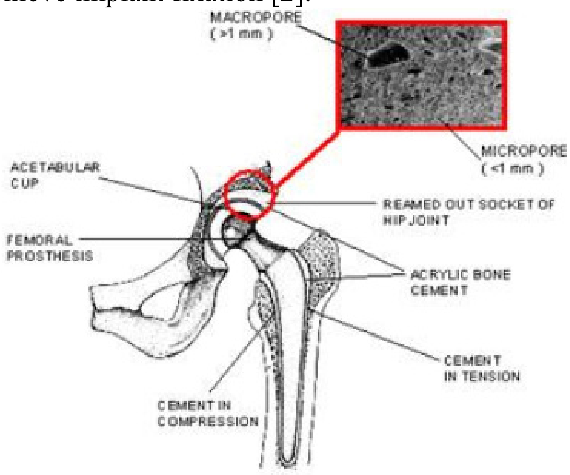

Figure 1. Schematic view of total hip replacement [3]

Some drawbacks associated with PMMA-based bone cements are: local tissue damage due to chemical reactions during polymerization and strong exothermic setting reaction, the high shrinkage of the cement after polymerization, the stiffness mismatch between bone and the cement, toxic effect of the monomer, inability to bond directly to bone causing loosening at the interface and brittle nature [2]. Loose cement particles also mediate osteolysis of the bone and are highly unwanted. Special problems occur at the interfaces due to the different elastic module of the materials (110 GPa for titanium, 2.2 GPa for PMMA, and 20 GPa for bone) [3].

The role of the cement is directly related to the mechanical properties of the cement, especially the resistance to fracture of the cement in the mantle at the cement-prosthesis interface or the cement-bone interface. Method of cement mixing is very important since porosity is one of the crucial characteristics that determine its resistance to fracture. Cement that is inadequately mixed exhibits a high degree of porosity. High porosity means that number of pores is present acting as stress raisers and initiating spots for cracks, further promoting early fatigue failure. Number of types of bioactive bone cements has been investigated to overcome above listed problems.

PMMA is one of the polymeric materials also used as matrix for carbon fibers composites [1]. Carbon fiber has been recognized, recently, as a material with many exciting applications in medicine, since they, when used as a reinforcing material significantly enhance the mechanical properties of the observed system. Orientation and fiber content can be varied in such a way to provide the implant with mechanical property needed for proper functioning. One common feature that implant must satisfy is its resistance to fatigue failure and to be resistant to attacks from the physiological environment [1]. Many new approaches have been tried to enhance mechanical properties of PMMA bone cements [4,5]. Recent methods include addition of reinforcing particle or fiber in order to increase cement stiffness, strength and toughness [4]. Common approach considers improvement of fatigue characteristics, by reinforcement of PMMA with carbon fibers, hydroxyapatite particles, stainless steel fibers, titanium fibers or zirconia particles or fibers, etc.

A recognized issue is that it is not always possible to distinguish the medical-grade polymers from the conventional polymers. They are selected based on clean condition or trace element analysis or mechanical properties. Processing involve clean room conditions and special care not to contaminate the materials.

The ready bone cement is a compound consisting of 90% of polymethylmetacrylate**,** (PMMA), which exists in an amorphous state and is completely transparent. The rest are mainly crystals of barium sulfate or Zirconium oxide that make the resulting product radio-opaque. The microscopic structure of bone cement is made by two substances glued together. One part consists of the small particles of pre-polymerized PMMA (PolyMethylMetaAcrylate), so called “pearls”. These pearls are supplied as a white powder. The other substance is a liquid monomer of MMA (MethylMetacrylate). Both substances are mixed together at the operation table with added catalyst that starts the polymerization of the monomer fluid. Amorphous polymers such as PMMA are brittle, hard plastics at room temperature [6]. It is isotropic and significantly bioinert material. PMMA is attacked by mineral acids but is resistant to alkalis, water and most aqueous inorganic salt solutions [6]. PMMA is also subject to both elastic and viscoelastic (creep) deformation under load [7]. Considering previously stated, it is very important to properly define mechanical characteristics of PMMA bone cements, to be able to further enhance their features.

Characterization of bone cement to cyclical loading is extremely significant and is a subject of many ongoing studies [8-14]. For instance, if total hip replacement is considered, many daily activities involve many cycles of different alternating loading patterns (walking, etc.). Studies showed that one of the main reasons of cement failure mechanism is related to fatigue failure and fatigue crack propagation [8]. Indentation represents flexible mechanical testing due to its simplicity, minimal specimen preparation. It allows selection of loads and tip geometry. Forces can be applied from kilo-newtons down to nano-newtons, but also displacements down to nanometer. Indentation response is related to specific aspects of materials in question (porous structure, biomaterials, etc.) and interpretation of results requires specific knowledge about indentation mechanics and physics of the observed material [15]. The hardness of a material is usually defined as the resistance to local deformation [15]. Until development of instrumentation to accurately measure imprint dimensions (contact area) after unloading, hardness tests were limited to macro scales. However, since great advancements in this area, micro and nano scale optical measurements are widely available thus leading to expansion of indentation interpretation. Devices with depth sensing possibilities, such as CSM Nano Indentation Tester, enable determination of hardness, elastic modulus, plastic stress-strain behavior and/or creep behavior directly using the tester, without the need to measure contact impressions.

2. PRINCIPLE OF INSTRUMENTED INDENTATION TESTING (IIT)

The Nano Indentation Tester uses an already established method where an indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load. When reaching a pre-set maximum value, the normal load is reduced until partial or complete relaxation occurs. This procedure is performed repetitively; at each stage of the experiment the position of the indenter relative to the sample surface is precisely monitored with a differential capacitive sensor. For each loading/unloading cycle, the applied load value is plotted with respect to the corresponding position of the indenter. The resulting load/displacement curves (Fig. 2) provide data specific to the mechanical nature of the material under examination. Established models are used to calculate quantitative hardness and elastic modulus values for such data.

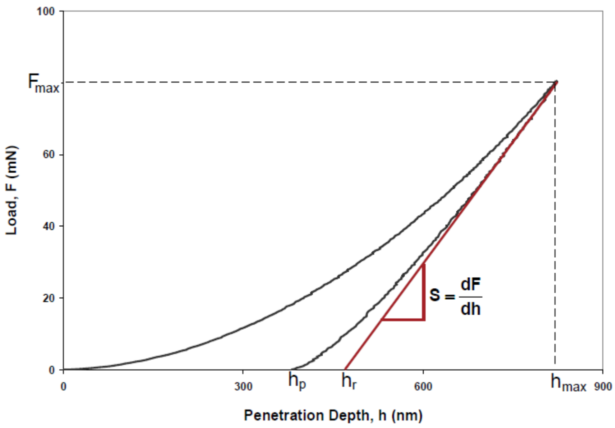

Figure 2. Typical Load/displacement curve

Evaluation of elastic modulus and hardness using instrumented indentation is realised by the method developed and proposed by Oliver and Pharr. It is the most common approach to determine hardness and modulus by interpretation of load - penetration depth (F - h) behavior during indentation (Fig. 1). Oliver and Pharr developed Power Law Method that describes the upper portion of the unloading curve by a power law relationship:

$$F = F_{max}\left(\frac{h - h_p}{h_{max} - h_p}\right)^m$$

where,

F - is the test force,
Fmax - is the maximum applied force,
h - is the indentation depth under applied test force,
hp - is the permanent indentation depth after the removal of the test force,
hmax - is the maximum indentation depth at Fmax,
m - is a power law constant exponent.

The power law exponent *m* is determined by a least squares fitting procedure and is a function of the indenter geometry.

The contact stiffness *S* is given by the derivative at peak load:

$$S = \left(\frac{dF}{dh}\right)_{max} = m \cdot F_{max}(h_{max} - h_p)^{-1}$$

And the tangent depth, *h*r, is thus given by:

$$h_r = h_{max} - \frac{F_{max}}{S}$$

Where h_r is the point of intersection of the tangent c to curve b at F_{max} with the indentation depth-axis. The contact depth (depth of the contact of the indenter with the test piece at F*max*), h_c, is then:

$$h_c = h_{max} - \varepsilon(h_{max} - h_r)$$

where ε depends on the power law exponent *m*.

The Indentation Testing Hardness H_{IT} is determined from the maximum load, F_{max}, divided by the projected contact area A_p at the contact depth h_c :

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

Where hc is the depth of the contact of the indenter with the test piece at F_{max}. A_p (h_c) is the projected area of contact of the indenter at distance h_c from the tip. A_p is a function of the contact depth h_c and is determined by a calibration of the indenter tip.

The Vickers Hardness HV is defined by:

$$HV = \frac{F_{max}}{9.81 \cdot A_c(h_c)}$$

Where *Ac* is the developed contact area and can be calculated from the projected contact area A_p and the indenter geometry as:

$$A_c = \frac{A_p}{\sin\alpha}$$

Where α is the angle between the axis of the diamond pyramid and its faces, α = 68° for a Vickers indenter (Fig. 3) and α = 65.27° for a modified Berkovich indenter.

For Vickers indenter: HV = 0.0945 H_{IT}
For modified Berkovich indenter: HV = 0.0926 H_{IT}

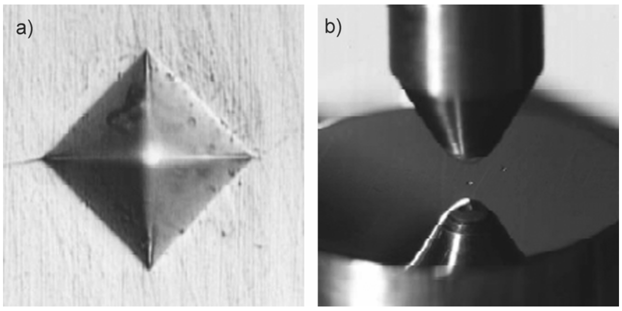

Figure 3. CSM Micro instrumented indentation testing: a) Optical micrograph of a Vickers indentation into a standard steel reference sample; b) Detail of Vickers indenter mounted above sample

Indentation Modulus E_{IT}

The reduced modulus of the indentation contact, E_r, is given by:

$$E_r = \frac{\sqrt{\pi} \cdot S}{2 \cdot \beta \cdot \sqrt{A_p(h_c)}}$$

Where β is a geometric factor depending on the diamond shape (circular: β = 1, triangular: β = 1.034, square: β = 1.012). The Young's modulus of the sample, E_{IT}, can then be obtained from:

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_{IT}} + \frac{1-\nu_i^2}{E_i}$$

Where
ν_i is the Poisson's ratio of the indenter.
ν_s is the Poisson's ratio of the sample.
E_i is the modulus of the indenter.

3. EXPERIMENTAL TEST

Bone cement prepared from commercially available type of mixture was used as a sample material for indentation tests. PMMA is isotropic, showing no crystallinity, elasto-viscoplastic solid and amorphous polymer. Several indentations have been performed on each sample using the CSM Micro Indentation Tester (Fig. 4). Indentation test lasted for 300 cycles. Tests were performed with maximum normal load of 15 N, minimum load of 5 N and approach speed of 5000 nm/min.

Vickers indenter was applied with quadratic loading type. There was no pause at maximum load before unloading. Displacement measurements were realised using LVDT sensor which is a part of the tester. Maximum possible indentation depth was limited to 200 μm with displacement resolution of 0.3 nm.

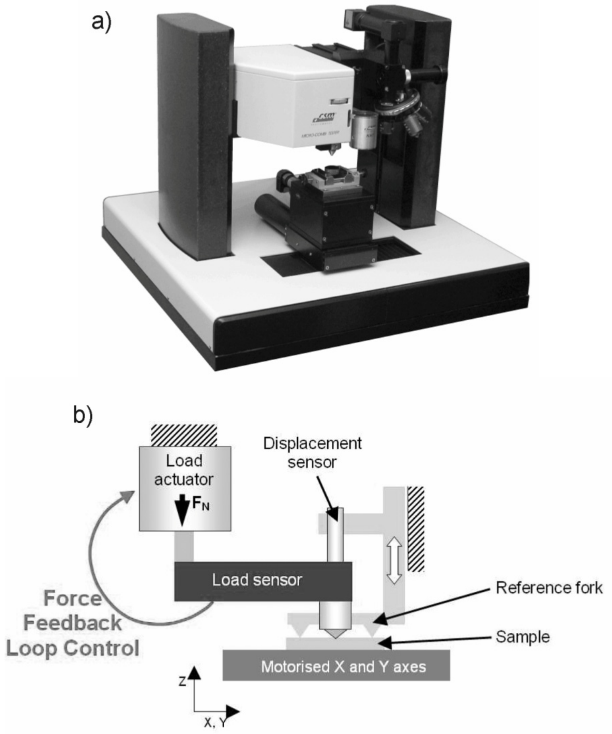

Figure 4. a) CSM Micro Indentation Tester
b) Schematic view of the main elements of Micro Indentation Tester

4. RESULTS AND DISCUSSION

Indentation curve, that is, diagram of the normal force applied during micro indentation as a function of the number of cycles is shown in Fig. 5. This is classical fatigue mode of indentation testing, whereas the force is loaded and unloaded constantly during indentation without a pause. Material is subjected to constant load/unload pattern and is not left to rest, such as in case of indentation mode of testing on creep.

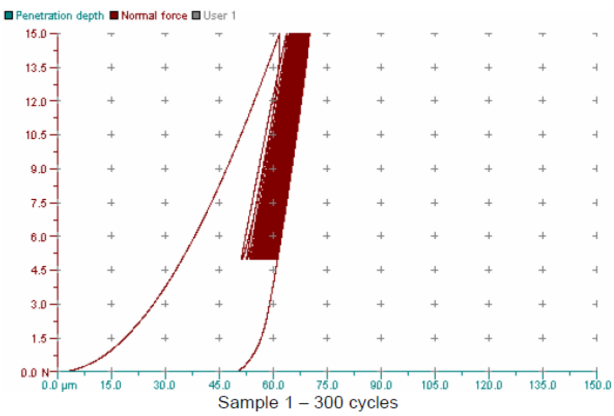

Figure 5. Normal force versus penetration depth curve during micro indentation

Imprint on bone cement sample after indentation lasting for 300 cycles, is shown in Fig. 6. Typical pattern produced by Vickers indentation is clearly seen. Detailed view of the left lower angle is shown in Fig. 6b. The imprint is well shaped with clearly developed edges and no microcracks around angles. This is in consistence with the fact that amorphous materials usually present an elastic behavior up to failure [16]. Permanent deformation occurs due to high shear and compressive stresses which are both present in highly localized area.

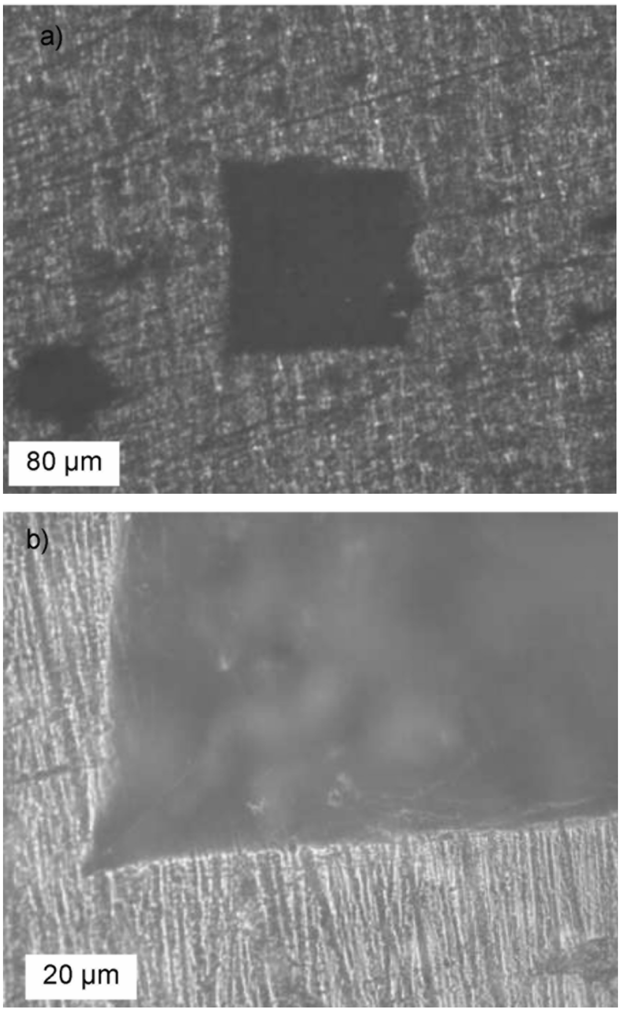

Figure 6. a) Micrograph of the indentation imprint on bone cement after 300 cycles, b) Detail of the indentation imprint on PMMA after 300 cycles (left bottom angle)

Calculated values of hardness H_{IT} and elastic modulus E_{IT} of bone cement sample after 300 cycles obtained by the indentation tester is shown in Table 1.

Table 1. Values of hardness H_{IT} and elastic modulus E_{IT} of bone cement sample after 300 cycles obtained by the indentation tester

	Value for PMMA sample after 300 cycles
Hardness, H_{IT} [MPa]	162.84
Elastic modulus, E_{IT} [GPa]	2.74

Hardness profile and elasticity profile during multicycling loading, unloading and reloading are shown in Fig. 7. Values given in Table 1 are automatically calculated by the tester according to Oliver and Pharr approach, by analysing the unloading curves (Fig. 5). It can be clearly seen that E_{IT} value is rather uniform, whereas hardness has slightly decreasing trend.

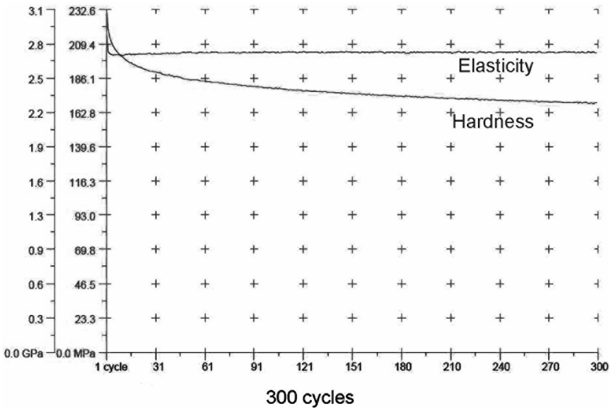

Figure 7. Hardness, H_{IT} and elasticity, as a function of the number of cycles during micro indentation

Loosening is recognized as one of the primary sources of total hip replacement failure. One of the main reasons is considered to be fatigue failure of the implant-bone cement and bone cement - bone interface. That is the reason why characterization of bone cement to cyclical loading is extremely significant and is a subject of many ongoing studies [8-14]. Also, PMMA has been widely used as a model for studies of fatigue and fracture in polymers. Effects of different factors have been investigated, whereas variable amplitude loading offer insight in its behavior from aspects of fatigue and crack propagation. The loading curve in Fig. 5 consists of both elastic and plastic contribution, while the unloading curve is purely elastic and allows calculations of elastic modulus and hardness. Bone cements have a more complicated structure if compared to pure PMMA, with previously polymerised beads in a softer matrix which cures on implantation, and other components such as particles of barium sulphate or zirconia to make the cement visible in radiographs. This microstructural complexity means that the cement may behave very differently from pure PMMA. There are several commercially available bone cement mixtures and they have been comprehensively studied both in laboratory and clinical practice. However, there are still features that need to be enhanced and indentation tests can be used for further understanding of its behavior. Clinical failure of the cement occurs over long time periods, and this implies that the crack growth rate is very low, perhaps as low as 10^{-12} m/cycle. It is clear from Fig. 6 that cracks did not occur in this testing and that edges are smooth and clearly marked with well shaped imprint. Therefore, values of hardness H_{IT} and elastic modulus E_{IT} of bone cement sample can be taken as valid. Micro indentation method can be used for measuring of elastic modulus and hardness of prepared bone cement mixtures in a short period of time.

5. CONCLUSION

Characterization of bone cement to cyclical loading is extremely significant and is a subject of many ongoing studies. Studies showed that one of the main reasons of cement failure mechanism is related to fatigue failure and fatigue crack propagation. Indentation represents flexible mechanical testing due to its simplicity, minimal specimen preparation and short time needed for tests. Devices with depth sensing possibilities, such as CSM Nano Indentation Tester, enable determination of hardness, elastic modulus, plastic stress-strain behavior and/or creep behavior directly using the tester, without the need to measure contact impressions.

Results obtained within this study were fully comparable with the literature data found for PMMA and commercial bone cements. Micro indentation method can be used for measuring of elastic modulus and hardness of prepared bone cement mixtures. Very important feature of CSM Micro indenter is automatic recording of optical photographs of realised imprints.

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