Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 20
ISSUES 1-2
January-February
2007

Stiffness and strength of composite acrylic bone cements

I. Knets*, V. Krilova, R. Cimdins, L. Berzina, V. Vitins
Institute of Biomaterials and Biomechanics, Riga Technical University,
Kalku iela 1, Riga LV1658, Latvia
* Corresponding author: E-mail address: knets@latnet.lv

Received 31.10.2006; accepted in revised form 15.11.2006

Materials

ABSTRACT

Purpose: Different acrylic bone cements based upon PMMA-MMA system are applicable for implant fixation in bone tissue. The aim of present study is the optimisation of the structure of some new bone acrylic cements made on the basis of PMMA-ethylmethacrylate-triethyleneglycoldimethacrylate and bone cements having additives (HA and radio pacifier), and the finding of the effect of these modifications on the flexural strength and stiffness.
Design/methodology/approach: Different new bone cements on the basis of PMMA-EMA-TEGDMA system (ABC) were developed experimentally. The stiffness and strength of the samples of these modified cements were determined in the special three point bending equipment.
Findings: A comparison of the flexural properties of new PMMA-EMA-TEGDMA cements and commercial available PMMA-MMA cement showed that commercial bone cement had larger values of ultimate strength and modulus of elasticity, but the difference is not very important. As concerns the polymerisation peak temperature, then there is a significant difference between commercial PMMA-MMA cement (~ 800C) and PMMA-EMA-TEGDMA modified cements (50 – 600C). The introduction of 10% and 18% of HA into solid phase does not influence essentially strength and modulus of elasticity of the PMMA-EMA-TEGDMA bone cements. The introduction of radio pacifier BaSO4 into bone cement leads to flexural strength diminishing. Low polymerisation peak temperature and appropriate mechanical properties of bone cements developed allows regarding new 3-D structure acrylic bone cements as promising biomaterials.
Research limitations/implications: It is supposed to carry out animal testing to learn more about reaction of modified implanted material on the biological environment.
Practical implications: The new materials could be efficiently used as bone cements because they will not damage surrounding biological tissue during curing.
Originality/value: Paper is providing the new information about possibilities to realize the safe fixation of implants.
Keywords: Biomaterials; Bone cement; Stiffness; Strength

1. Introduction

It is very important for understanding the mechanical behaviour of materials to know their chemical composition, structure, mechanical properties and their dependence upon technology parameters [1-7].

A phenomenon of men life expectancy is connected with prolonged functioning of all body organs. Nevertheless man skeleton is subjected to essential change, and an injured bone replacement by implant is the way to enhance the quality of life. Bone cements of different composition are used for implant fixation in bone tissue. Acrylic bone cements are the most applicable for this purpose.

The most of commercially available acrylic bone cements are based upon PMMA-MMA system. These cements are widely used in bone restorative and replacement surgery for forty years with good clinical results. However, the cements have some well-

known drawbacks, such as high polymerisation temperature, large shrinkage, brittleness and some others.
Polymerisation peak temperature can achieve 80 - 90^{0}C and this temperature shock is considered to be the reason of surrounding tissues necrosis [8].

Substitution of PMMA-MMA system completely or partially by other components is the subject of investigation of many scientific centres for many years.

Bone cement based upon poly(ethylmethacrylate)-n-butylmeth-acrylate (PEMA-BMA) was developed in Bonar Cole Polymers Ltd and the London Hospital Medical College [9], and this system has advantages over PMMA-MMA system including the biomechanical properties. Polymerisation peak temperature is much lower (50 - 60^{0}C); the cement has high ductility [8].
The flexural strength and stiffness of the cement were increased by addition of up to 40% hydroxyapatite (HA) particles. The flexural strength was increased from 29.3(±0.54) MPa to 43.3(±1.75) MPa and the flexural modulus of elasticity - from 835(±95.5) MPa to 1746(±43.7) MPa [10].

The introduction of cross-linking agents into the PEMA-BMA cement led to ultimate tensile strength increase from 25.0(±0.2) MPa to 30.0(±0.51) MPa and modulus of elasticity increase from 700(±210) MPa to 2190(±370) MPa for cement with 5% triethyleneglycoldimethacrylate (TEGDMA) [11].

Earlier we have developed new acrylic bone cements with 3-D structure on the base of PMMA in solid phase and ethylmethacrylate (EM)-TEGDMA or EM-ethylenedimeth-acrylate in liquid one [12]. The basic bone cements were modified by introduction of hydrophilic and hydrophobic co-monomers into liquid phase [13] and blending PMMA with P(MMA-n-hexylacrylate) or P(MMA-2-ethylhexylmethacrylate) [14]. The cements have essentially lower polymerisation peak temperature as compared with PMMA-MMA bone cements. The handling properties improvement, the diminishing of holes formation risk and model substance sorption ability was taken into account.

The aim of present study is the further optimisation of bone cement structure and composition and their correlation with flexural properties of developed cements.

2. Materials and methodology

MMA, EMA, n-hexylacrylate (HexA), 2-ethylhexylmethacrylate (EHMA) and methacrylic acid (MAA) (all ALDRICH) were purified by vacuum distillation.

TEGDMA, N,N-dimethyl-p-toluidine (DMT) (ALDRICH) and benzoyl peroxide (BP) (FLUKA) were used as received.

PMMA and P(MMA-HexA) were synthesized as spherical beads of 40 – 100 μm diameters by suspension polymerisation.

HA (ALDRICH) was pounded and sieved, fractions 40 - 90 μm and < 40 μm were taken.

$BaSO_4$ (pharm., for roentgenoscopy) (ЭКРОС) was sieved and fraction < 40 μm was taken.

To form bone cement specimens the ratio of solid phase to liquid phase was from 1g per 0.36 ml till 1g per 0.435 ml for bone cements of PMMA-EMA-TEGDMA basic system and 1g per 0.48 ml for commercial bone cement based upon PMMA-MMA system.

The content of DMT in liquid phase of bone cement PMMA-EMA-TEGDMA system was 0.7 %; the content of BP in solid phase was about 1 %.

Solid and liquid phases were mixed during 1 min and after waiting time about 4 min mixture was placed into moulds. For mechanical tests specimens were formed as rectangular bars and aged in dry condition.

The polymerisation peak temperature was measured using Checktemp 1 (HANNA Instr.), resolution 0.1^{0}C, and accuracy ± 0.3^{0}C.

Mechanical experiment - flexural testing was conducted on a universal testing machine (PC controlled INSTRON 4301 with series IX software). A three-point bending fixture was used. Flexural modulus of elasticity and flexural strength (maximum flexural stress in the specimen at the moment of fracture) were determined for the bone cement specimens (5 x 5 x 50 mm) on span 35 - mm; tests proceeded until specimens had fractured.

3. Results and discussion

Acrylic bone cement formation is radical polymerisation process which takes place in the presence of dissolved and none dissolved polymer of similar to formed or another structure and, in some cases, in the presence of additives.

Polymerisation reaction of acrylic monomers is exothermic process with more or less expressed auto acceleration stage; therefore bone cement formation is accompanied by temperature growth, the level of which depends on process enthalpy and heat capacity of the system.

The new bone cements (ABC) made on the base of PMMA-EMA-TEGDMA system have relatively low polymerisation peak temperature, and chemical modification of this system allows to improve also the other properties of the cement. The evaluation of mechanical properties, in particular, flexural strength and flexural modulus of elasticity, of these modified bone cements is the necessary step towards development of bone cement with optimal properties. Bone cements in flexural tests exhibited a linear response of material.

The introduction of co-monomers having high hydrophilic and hydrophobic character (MAA and HexA) into the liquid phase did not influence essentially the flexural strength value, as well as flexural modulus of formed bone cement (Table 1).

The influence of bone cement solid phase morphology on bone cement properties is little discussed question. In particular co-polymer porosity might influence bone cement formation process at least via:

- gas presence in (co) polymer pores;
- polymer dissolution degree change in liquid phase;
- ratio solid phase: liquid phase change necessity.

Porous PMMA dispersion has been synthesized and blended with PMMA beads of bulk structure. The porosity level has been evaluated via polymer blend apparent density [14].

Presence of pores noticeably decreases the flexural modulus of elasticity, but an influence to the flexural strength is insignificant (Table 2).

Table 1.
Flexural strength and flexural modulus of elasticity of the bone cements with co-monomers and without them [mean (± standard deviation)]

Bone cement*	Flexural strength, MPa	Flexural modulus , MPa
ABC-M2	51.5±2.5	1222±119
ABC	49.3±2.1	1255±59

*content of TEGDMA was 8% in liquid phases; ABC-M2 contained 1% MAA and 10% HexA in liquid phase; specimens were aged 2 month.
P.S. Data in all tables have been obtained during present investigation.

Table 2.
The dependence of flexural strength and flexural modulus of elasticity from apparent density of bone cement solid phase [mean (± standard deviation)]

Bone cement *	Apparent density, g/ml	Flexural strength, MPa	Flexural modulus of elasticity, MPa
ABC-M2	0.53	39.8±3.1	1295±210
ABC-M2	0.73	39.9±1.9	1666±172
ABC-M3	0.52	36.9±2.1	1076±194
ABC-M3	0.55	39.1±2.2	1178±281
ABC-M3	0.70	44.1±4.2	1581±167

*- content of TEGDMA was 8% in liquid phases;
ABC-M2 contained 1% MAA and 10% HexA in liquid phase; ABC-M3 contained 1% MAA and 10% EHMA in liquid phase; ageing – 3 month.

Table 3.
Flexural strength and flexural modulus of elasticity of bone cement ABC-M2 before and after chemical modification of its solid phase * [mean (± standard deviation)]

P(MMA-HexA) content in solid phase	Flexural strength, MPa	Flexural modulus, MPa
0	36.5±6.1	1650±259
15	36.8±0.8	1703±153

*- ageing – about 6 month.

Table 4.
Flexural strength and flexural modulus of elasticity of bone cement with and without HA* [mean (± standard deviation)]

Content of HA in solid phase	Flexural strength, MPa	Flexural modulus of elasticity, MPa
10	46.9±2.8	1392(±86)
10 **	46.6±3.1	1535(±220)
18	45.7±7.8	1635(±249)
0	43.8±6.8	1447(124)

* solid phase of all specimens contained 25% P(MMA-HexA); HA fraction 40 - 90 μm; ageing - 1 week;
** HA fraction < 40 μm.

Table 5.
The influence of $BaSO_4$ on the flexural strength and flexural modulus of elasticity of bone cements [mean (± standard deviation)]

Bone cements	Flexural strength, MPa	Flexural modulus of elasticity, MPa
ABC*	43.8±6.8	1477±124
ABC+10 %$BaSO_4$ *	35.6±6.4	1491±86
PMMA-MMA+9%$BaSO_4$	48.9±10.6	1617±108

* solid phase contained 25% P(MMA-HexA); ageing - 1 week.

It might be noted that not a significant decrease of measured mechanical parameters of bone cement has been found with the increase of small pores in the solid phase of cement. Alternatively, large pores created during the bone cement formation (curing) influences the mechanical parameters in much larger extent.

Porous structure and, accordingly, the decrease of apparent density of bone cement solid phase determine the some growth of liquid phase volume. This factor is responsible for polymerisation peak temperature growth [14]. Taking into account also the decrease of the modulus of elasticity, more dense PMMA dispersion is preferable from these points of view.

The modification of bone cement solid phase by blending PMMA with P(MMA-HexA) beads in order to achieve better handling properties practically does not influence the values of flexural strength and flexural modulus of elasticity (Table 3).

To achieve better biocompatibility of bone cement, HA is known to be a useful additive [10]. The introduction of 10 % and 18% HA into modified solid phase of bone cement did not influence essentially its flexural properties (Table 4).

Smaller fraction of HA also gave not any difference. Surgery application of bone cement demands the X-ray control of implant, and $BaSO_4$ is usually used as radio pacifier. It is known that the introduction of this radio pacifier into bone cement solid phase is diminishing the mechanical strength [15]. Our material ABC with radio pacifier also has diminished flexural strength, but flexural modulus of elasticity practically did not change (Table 5). The comparison of flexural properties of ABC tested and commercial bone cement (PMMA-MMA) showed that commercial bone cement had larger values of ultimate strength and modulus of elasticity, but this difference is not large. As to polymerisation peak temperature, there is large difference between commercial PMMA-MMA cement (~ 80^0C) and ABC modified cements (50 - 60^0C).

4. Conclusions

The comparison of the flexural properties of newly developed bone cement (ABC) and the commercial bone cement (PMMA-MMA) showed that commercial bone cement had larger values of flexural strength and modulus of elasticity, but this difference is not significant.

As concerns the polymerisation peak temperature, then for modified cements ABC it is much less (50 - 60^0C) than for commercial bone cement PMMA-MMA (~ 80^0C).

References

[1] L.A. Dobrzanski, Synergic effects of the scientific cooperation in the field of materials and manufacturing engineering, Journal of Achievements in Materials and Manufacturing Engineering, 2006, Vol. 15, 9-20.

[2] M. Kciuk, The structure, mechanical properties and corrosion resistance of aluminum AlMg1Si1 alloy, Journal of Achievements in Materials and Manufacturing Engineering, 2006, Vol. 16, 51-62.

[3] M. Adamiak, Selected properties of the aluminum alloy base composites reinforced with intermetallic particles, Journal of Achievements in Materials and Manufacturing Engineering, 2006, Vol. 14, 43-47.

[4] J. Mialski, Properties of laminates containing polymer glass fiber recyclates, Journal of Achievements in Materials and Manufacturing Engineering, 2006, Vol. 14, 54-58.

[5] L.A. Dobrzanski, B. Ziebowicz, M. Drak, Mechanical properties and the structure of magnetic composite materials, Journal of Achievements in Materials and Manufacturing Engineering, 2006, Vol. 18, 79-82.

[6] I. Knets, Peculiarities of the structure and mechanical properties of biological tissue, Meccanica (Kluwer Academic Publ.), 2002, Vol. 37, 375-384.

[7] I. Knets, General principles in the bone tissue testing, Acta of Bioengineering and Computing, 1999, No 2, 55-66.

[8] J. Goodwin, M. Braden, S. Downes, N.J. Marshall, A comparison between two methacrylate cements as delivery systems for bioactive human growth hormone. Journal of . Material Science. Materials in Medicine, 1995, 6, 590-596.

[9] L.G. Wood, M. Braden, Bone cement. Pat.EP 0218471 A1 (01 Oct 1986).

[10] E.J. Harper, J.C. Behiri, W. Bonfield, Flexural and fatique properties of a bone cement based upon polyethylmeth-acrylate and hydroxyapatite. Journal of Material Science. Materials in Medicine, 1995, 6, 799-803.

[11] S. Deb, M. Braden, W. Bonfield, Effect of crosslinking agents on poly(ethylmethacrylate) bone cements. Journal of Material Science. Materials in Medicine, 1997, 8, 829-833.

[12] V. Krylova, R. Cimdins, L. Berzina, V. Kasjanov, Acrylic composites for bone cements with three-dimensional polymer network structure. The Latvian Chemistry Journal, 2000, Nr.2, 81-88 (in Latvian with a summary in English).

[13] V. Krylova, L. Berzina, R. Cimdins, Modified cross-linked acrylic bone cements. In: Scientific Proceedings of Riga Technical University; Series: Material Science and Applied Chemistry, Riga, 2002, Nr4, 17-21.

[14] V. Krylova, L. Berzina, R. Cimdins. Structural modification of bone cement solid phase. In: Scientific Proceedings of Riga Technical University; Series: Material Science and Applied Chemistry, Riga, 2002, Nr.4, 65-71.

[15] S. Deb, B. Vazquez, The effect of cross-linking agents on acrylic bone cements containing radiopacifiers. Biomaterials, 2001, 22(15), 2177-2181.