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PMMA-based composite materials with reactive ceramic fillers

Part III: *Radiopacifying particle-reinforced bone cements*

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New acrylic bone cements were prepared from alumina particles previously treated by 3-(trimethoxysilyl)propylmethacrylate (γ-MPS), able to act both as radiopacifying and reinforcing agents. The present study deals with the handling characteristics and the compressive behavior of such cements. The influence of the particles morphology, their surface-modification by γ-MPS bonding agent, their concentration in the cement, the powder-to-liquid ratio and the benzoyl peroxide concentration are reported. The role of grafted γ-MPS molecules as coupling agent was confirmed. For several formulations, compressive strength and modulus reached 150 MPa and 3400 MPa respectively. Limitations in the use of such formulations are also comprehensively discussed.

1. Introduction

Since the work by Charnley in the early 1960s, acrylic cements led to the development of a successful technique in orthopaedic surgery for the fixation of joint prostheses to bone [1–3]. Originally developed for use as a dental material, acrylic bone cements consist of self-curing polymethylmethacrylate (PMMA), prepared by mixing the liquid part and the solid one of the unit. The liquid part contains three basic components: MMA monomer (97 vol %), an inhibitor for preventing the premature polymerization of the monomer and a promoter of the initiator decomposition. The solid phase consists of pre-polymerized PMMA beads (89 wt %), a mineral powder, such as barium sulfate or zirconium dioxide (10 wt %) acting as radiopacifier and a free-radical initiator (typically benzoyl peroxide, BPO).

By the end of the century, the total number of patients with cemented joint implants could be about 10 million, world-wide and for the 40-year period [4] (over 80% of hip and over 90% of knee-replacements [5]). The main advantages of this technique lay in the excellent primary fixation, in the load distribution between the implant and the bone, and in the fact that the technique allows a fast recovery of the patient. However, aseptic loosening concerns about 10% of the patients, who may need revision in less than 10 years after implantation. The mechanical failure of the cement or the osteolysis caused by the foreign body reaction induced by wear particles and debris are sometimes invoked [4].

While cementless fixation has not yet been able to replace bone cement for all pathological cases, an extensive research effort is still being devoted to achieve a longer life in service and to avoid premature loosening. The conventional hand-mixing technique has been optimized in order to reduce porosity: mechanical, ultrasound or vacuum mixing, pressurization or centrifugation of the mixture [6, 7]. Matrix modifications concern both the use of alternative monomers (or comonomers) and polymers or the addition of cross-linking agents, for adjusting the mechanical properties (compressive strength and modulus, creep strain and fracture toughness) [4]. Nevertheless the main path has been the reinforcement of the matrix with fillers [4]. The mixing with hard particles (glass beads, bioactive glass ceramic particles, inorganic bone and demineralized bone matrix, hydroxyapatite) or tough or rubber-toughened particles (ABS copolymer) has been studied. Other authors have used metallic fibers (stainless steel or tough titanium), polymeric fibers (aramid Kevlar®, polyethylene or PMMA) and carbon fibers [4]. Moreover, fiber reinforcement affects the distribution of load from the metallic implant to the surrounding [8] and, therefore, the lower strengthening efficiency in particle-reinforced cement allows a better match with the

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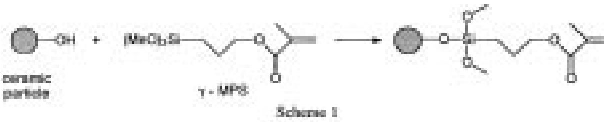
surrounding materials [9]. One of the main results that emerges from the fractographic analyzes described in these studies, is the lack of adhesion between the acrylic matrix and the fillers.

Our approach for enhancing the properties of bone cements and reducing the production of wear particles and debris was directed towards the mechanical reinforcement through the radiopacifier particles. Our idea consists of improving the interface adhesion by establishing covalent chemical bonding between the inorganic fillers (oxide particles) and the PMMA matrix. This can be achieved through the preliminary treatment of the fillers surface with a silane bonding agent (Scheme 1), as 3-(trimethoxysilyl)propylmethacrylate (γ-MPS), capable of later copolymerizing with the (co)monomers. It can be noticed that, in the orthopaedics-related literature, this approach has been rarely reported, although as early as 1978 Kusy recommended the use of coupling agents [10]. Cooke *et al.* reported that chemical coupling of the radiopacifier ZrO_2 particles to the PMMA matrix (induced by a previous surface glow discharge polymerization with various monomers) increases the tensile strength of the cement back to the values obtained for a cement without any radiopacifier filler [11]. Later, Behiri *et al.* studied polyethylmethacrylate-based cements reinforced with γ-MPS treated hydroxyapatite particles and they reported the enhancement of tensile modulus (+ 14%) and yield stress (+ 22%), when compared to untreated fillers [12]. Prior to silanation, the pre-treatment with a siliceous coating of the powder (from an aqueous solution of sodium metasilicate) led to further enhancement [13].



Scheme 1

The present study deals with the preparation and the mechanical characterization (compressive behavior) of acrylic cements prepared from γ-MPS treated alumina particles, which could act simultaneously as radiopacifying and reinforcing agents. This paper is the third of a series dealing with alumina/PMMA composites. The alumina surface modification by γ-MPS [14] and the study of the copolymerization reaction between grafted γ-MPS and free MMA [15] have already been reported.

2. Materials and methods

Radiopacifier particles were commercial alumina powder, whose physical properties are reported in Table I. 3-(trimethoxysilyl)propylmethacrylate (γ-MPS), 3-(acetoxypropyl)trimethoxysilane (γ-AcPS), toluene (99.8%), benzoyl peroxide (BPO), methylmethacrylate (MMA), n-butylmethacrylate (BuMA) and N,N-dimethyl-*p*-toluidine (DMT) from Sigma-Aldrich were used without further purification. The PMMA beads were supplied by the Ceraver-Ostéal company. They had a spherical shape with an average diameter of 60 µm and average molar masses $\overline{M_n} = 90\,000$ and $\overline{M_w} = 200\,000\,\mathrm{g\,mol^{-1}}$ (from size exclusion chromatography calibrated with polystyrene standards).

Silane grafting reactions onto alumina surface were carried out in toluene as previously described [14]. After dispersing 10 g of alumina powder in 200 ml of toluene, an excess of silane was added and the resulting solution refluxed for 15 h. The treated powders were then washed with 300 ml of fresh toluene in a Soxhlet apparatus for 24 h and then dried at 110 °C for 3 h under vacuum. Thermogravimetry (Setaram MTB 10–8) of 20–50 mg of modified powders was performed in static air at a ramp rate of $240\,^{\circ}\mathrm{C\,h^{-1}}$ to 650 °C. Surface densities of grafted molecules were determined from thermogravimetry results, according to calculations previously described [14].

PMMA beads, alumina particles and BPO were physically blended in a Fritsch miller for 30 min. The cements were prepared by hand-mixing the powder and the liquid part (according to the standard prescribed routine of clinical usage) and injecting the resulting paste in the dough state into cylindrical stainless-steel molds ($h = 18\,\mathrm{mm}; \Phi = 6\,\mathrm{mm}$). Stainless-steel plates on each end of the molds were firmly held with a C–clamp. After completed curing at room temperature, specimens were extracted from molds by a screw-jack and aged for 24 h at room temperature. The ends of the cylinders were surfaced plane at right angles to the axis. The final dimensions of the specimens followed the standards ISO 5833/1 for compression ($h = 12\,\mathrm{mm}; \Phi = 6\,\mathrm{mm}$). Ten specimens were prepared for each formulation. Those showing obvious structural defects or voids on visual inspection were discarded, leaving a minimum of eight specimens per batch suitable for testing.

The compressive stress-strain behaviors were determined at 25 °C by means of a 4466 Instron

TABLE I Physical properties and silanation results of commercial alumina powders and compressive behavior of acrylic bone cements containing 6.6 wt % of the silanated particles and prepared with a powder-to-liquid ratio equal to 2.5 by the mixing of $m_{\mathrm{BPO}} = 0.45\,\mathrm{g}$, $m_{\mathrm{PMMA}} = 41.75\,\mathrm{g}$, $m_{\mathrm{alumina}} = 4.3\,\mathrm{g}$, $V_{\mathrm{MMA}} = 16.9\,\mathrm{mL}$, $V_{\mathrm{BuMA}} = 2.7\,\mathrm{mL}$ and $V_{\mathrm{DMT}} = 0.4\,\mathrm{mL}$

Commercial name	GE1	GE30	CR30	C
Supplier	Baikowski Chimie	Baikowski Chimie	Baikowski Chimie	Degussa
Purity (%)	> 99.99	> 99.99	> 99.99	> 99.6
Crystallographic form	α	α	α	δ
Particle size d_{50} sedigraph (µm)	8.2	12.7	0.5	0.013
Specific surface area ($m^2 \cdot g^{-1}$)	3.9	25.5	26.6	100
γ-MPS surface density measured by TGA ($\mu\mathrm{mol} \cdot \mathrm{m}^{-2}$)	8.9	7.5	7.3	6.2
Surface developed by alumina particles in cement ($m^2 \cdot g^{-1}$)	0.26	1.7	1.8	6.6
Compressive strength (MPa)*	115 (2)	117 (2)	116 (2)	116 (2)
Compressive modulus (MPa)*	2270 (90)	2370 (50)	2440 (60)	2240 (110)

*The standard deviation is given in parenthesis.

electromechanical testing machine at a constant cross-head speed of 20 mm.min^{-1}. Alumina particles were extracted from cements by dissolution of the PMMA matrix in tetrahydrofuran, washed with 300 ml of fresh toluene in a Soxhlet apparatus for 24 h and then dried at 110 °C for 3 h under vacuum.

3. Results and discussion

The preparation process of a typical acrylic bone cement consists of the mixing of the liquid part with the solid one. Two phenomena take place simultaneously and both of them allow the control of the viscosity increase of the cement. The first one is a physical phenomenon and consists in the partial dissolution of PMMA beads by the liquid monomer. Therefore, the cement viscosity at the early stage of mixing is determined by the viscosity of this monomer-swollen materials. The second phenomenon is a chemical one and allows the viscosity increase during the setting dynamics. It results from the monomer polymerization initiated by the BPO decomposition accelerated by DMT. The resulting mechanical properties of the set cement depend on the cohesion between the polymerized monomer and the initial PMMA, that is to say depend on chain entanglement of the initial and the newly formed PMMA macromolecules [4].

The aim of this study concerns the effect of alumina radiopacifier particles on the setting process and the compressive behavior of the cured cements. Alumina was chosen because of its well-known biocompatibility [16]. Even if the electronic density of aluminum is lower than zirconium and barium, preliminary experiments showed that 4 wt % of alumina in cement is sufficient for providing a good opacity for X-rays. The influence of the particles morphology, their surface-modification by γ-MPS bonding agent, their mass concentration in the cement, the powder-to-liquid ratio and the BPO concentration are reported.

3.1. Effect of alumina particles morphology

The physical properties of the four selected commercial alumina powders and the amount of γ-MPS grafted onto their surface are shown in Table I. As demonstrated in a previous paper, the γ-MPS surface graft density is not dependent on either their crystallographic form or their specific surface area and is only restricted by the steric hindrance of the γ-methacryloylpropyl group [14,15].

Acrylic bone cements were prepared from various amounts of the γ-MPS grafted alumina particles and their setting behavior was carefully characterized according to the following terminology based on the cement viscosity in the dough state. A low-viscosity cement is fluid enough to be injected in molds with a syringe. A high-viscosity cement has to be handled with a spatula and the molds are filled by using gloved fingers. The cement is called unprocessable when at any moment during the setting process the materials can be molded without entrapment of large voids. The mixing of such a cement is difficult to perform because of its very high viscosity.

The observed setting behavior for each formulation is reported on Fig. 1. It appears that the higher the developed surface of the particles in the cement (Table I), the higher the initial viscosity of the cement. So, in cements where alumina concentrations were similar, the higher the specific surface area of the particles, the more important the monomer amount necessary for wetting the particles surface, and therefore the lower the monomer amount able to swell and partially dissolve the PMMA beads.

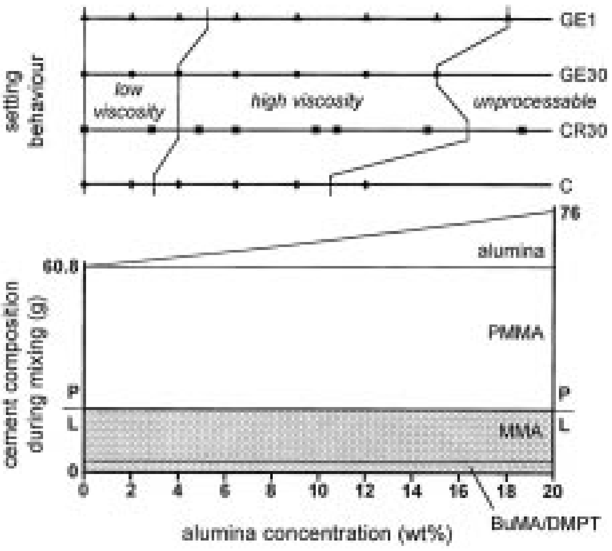


Figure 1 Setting behavior as a function of the alumina concentration for acrylic bone cements filled by γ-MPS grafted alumina particles GE1 (▲), GE30 (●), CR30 (■) and C (◆), prepared by the mixing of $m_{\mathrm{BPO}} = 0.45$ g, $m_{\mathrm{PMMA}} = 41.75$ g, $V_{\mathrm{MMA}} = 16.9$ mL, $V_{\mathrm{BuMA}} = 2.7$ mL and $V_{\mathrm{DMT}} = 0,4$ mL.

The results of compressive testing of set cements containing 6.6 wt % of the γ-MPS grafted alumina powders are reported in Table I. They show no major differences between the four batches, with an average compressive strength of 116 MPa and an average compressive modulus of 2300 MPa.

Consequently, only CR30 alumina powder was kept to carry out the study, because it appeared as a good compromise between compressive properties and a large range of concentration, thus allowing easy handling of the cement.

3.2. Effect of increasing alumina content

Setting behavior and compressive properties of cements obtained by increasing the amount of pristine CR30 alumina and γ-MPS grafted CR30 alumina are reported in Fig. 2. When alumina was silanated, the transition from low- to high-viscosity behavior occurred for a higher alumina concentration (6 wt % versus 3 wt % with pristine alumina). Indeed, with similar filler concentrations, the cement based on silanated particles showed a better mixing ability and the ease of handling was enhanced as compared to untreated alumina. Similar considerations were reported by Khorasani *et al.* [13]. So, the surface modification improves the compatibility of alumina with the organic matrix and decreases the liquid monomer amount needed for wetting the particle surface. The PMMA beads dissolution is better and the mixture has a lower viscosity.

Compressive strength and modulus increased with alumina content, whatever the chemical nature of its surface. Nevertheless, silanated powder led to better results, as observed previously with hydroxyapatite fillers

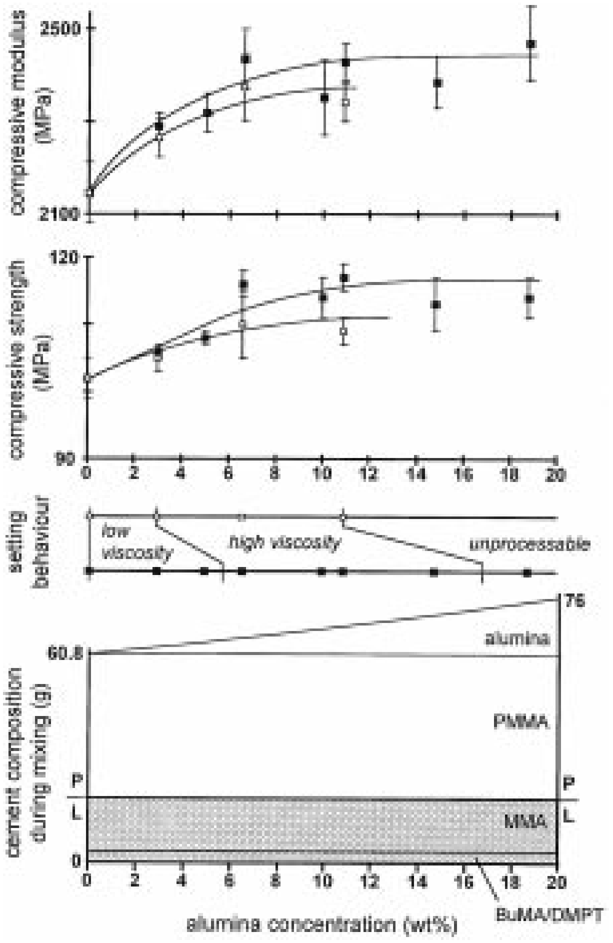


Figure 2 Compressive strength and modulus as a function of pristine CR30 alumina (□) and γ-MPS modified CR30 alumina (■) concentration for acrylic bone cements prepared by the mixing of $m_{\mathrm{BPO}} = 0.45\,\mathrm{g}$, $m_{\mathrm{PMMA}} = 41.75\,\mathrm{g}$, $V_{\mathrm{MMA}} = 16.9\,\mathrm{mL}$, $V_{\mathrm{BuMA}} = 2.7\,\mathrm{mL}$ and $V_{\mathrm{DMT}} = 0,4\,\mathrm{mL}$.

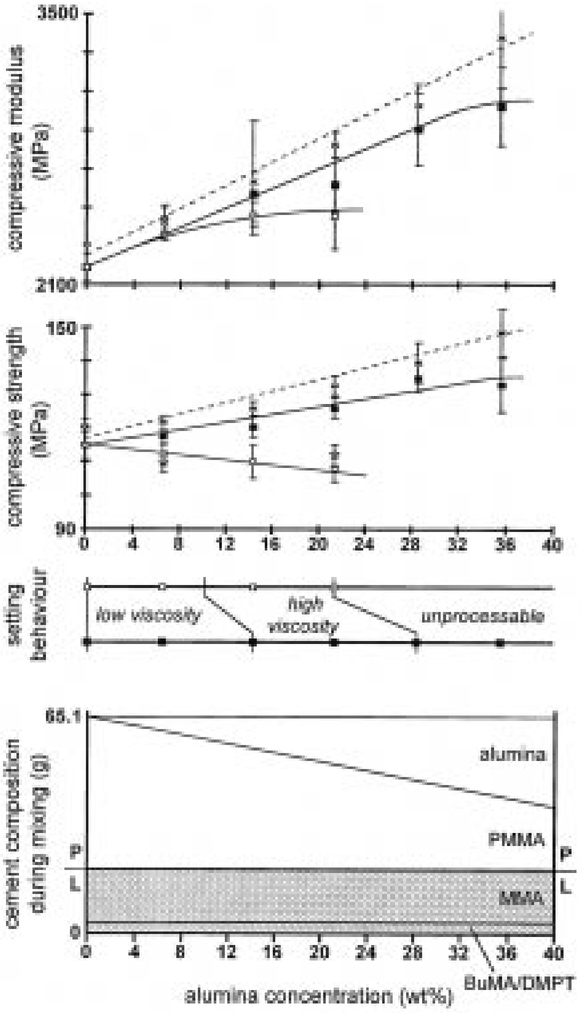


Figure 3 Compressive strength and modulus as a function of pristine CR30 alumina (□), γ-MPS modified CR30 alumina (■) and γ-AcPS modified CR30 alumina (☆) concentration for acrylic bone cements with powder-to-liquid ratio equal to 2.5 and prepared by the mixing of $m_{\mathrm{BPO}} = 0.45\,\mathrm{g}$ (0.7 wt %), $V_{\mathrm{MMA}} = 16.9\,\mathrm{mL}$, $V_{\mathrm{BuMA}} = 2.7\,\mathrm{mL}$ and $V_{\mathrm{DMT}} = 0,4\,\mathrm{mL}$. Further experiments (×) correspond to cements prepared with γ-MPS modified CR30 alumina and 1.4 wt % of BPO.

[12, 13]. A maximum compressive strength of 117 MPa and a maximum compressive modulus of 2450 MPa were obtained. But, beyond an alumina concentration of 8 wt %, the mechanical properties leveled off, because of the lack of homogeneity of the cement due to its very high viscosity and its laborious handling.

In order to improve the mechanical strength of the cements, it was necessary to increase the alumina content while keeping an easy handling of the mixture. This means using a sufficient amount of monomer for simultaneously wetting the alumina particles surface and swelling the PMMA beads, whatever the alumina concentration. So, new formulations were prepared with increasing amounts of alumina, but with a constant powder-to-liquid ratio equal to 2.5: PMMA beads were progressively replaced with an equivalent weight of alumina powder (Fig. 3). In such cases, handling was satisfactory up to 20 wt % of pristine alumina and 30 wt % of γ-MPS modified alumina. This phenomenon corroborates that the partial dissolution of PMMA beads is in competition with the wetting of alumina powder surface.

This once the evolution of compressive strength of cements as a function of alumina concentration showed two different behaviors between pristine alumina and surface-modified alumina. When alumina concentration increases, compressive strength increases for cement based on γ-MPS grafted particles, but decreases for cements based on pristine ones, as already observed by Cooke *et al.* [11]. The cement reinforcement with γ-MPS grafted particles allowed values of 135 MPa for compressive strength and 3025 MPa for compressive modulus to be reached.

3.3. Effect of varying powder-to-liquid ratio

In order to determine the optimum powder-to-liquid ratio (P/L), different batches were prepared with similar alumina concentration (14 wt %) by replacing PMMA beads with an equivalent weight of MMA (Fig. 4). So the chemical composition of cured cements were unchanged (in the hypothesis of a total monomer conversion for every batch). With each formulation, the viscosity of curing mixture was low. Nevertheless, when the powder-to-liquid ratio decreases, the polymerization kinetics slows down. For P/L ratio lower than 0.6, the cements were not hardened after 24 h at ambient temperature. This phenomenon results from the low viscosity of the mixture, which prevents the Trommsdorf-Norrish effect

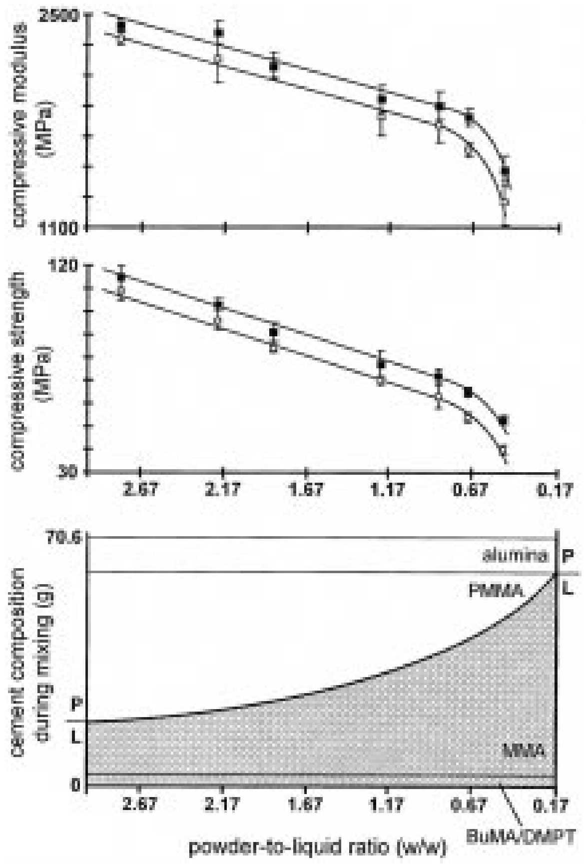


Figure 4 Compressive strength and modulus as a function of the powder-to-liquid ratio for acrylic bone cements with pristine CR30 alumina (□) and γ-MPS modified CR30 alumina (■) and prepared by the mixing of $m_{\mathrm{BPO}} = 0.45$ g, $m_{\mathrm{alumino}} = 9.9$ g (14 wt %), $V_{\mathrm{BuMA}} = 2.7$ mL and $V_{\mathrm{DMT}} = 0,4$ mL.

[4] to take place and therefore the monomer conversion to be complete.

The presence of residual monomers causes an internal plasticization effect and leads to more ductile materials. Compressive strength and modulus rapidly decrease with the powder-to-liquid ratio (Fig. 4) and, for P/L values lower than 0.7, the compressive strength was smaller than the minimum value required by ISO 5833/1 standard (70 MPa). Thus a minimum value of 2.5 for the powder-to-liquid ratio was found to yield good mechanical properties. Similar behavior was observed for both pristine and γ-MPS modified alumina: whatever the powder-to-liquid ratio, the chemical modification of alumina surface allowed compressive strength and modulus to gain *ca.* 10 and 160 MPa respectively.

3.4. Effect of benzoyl peroxide concentration

Vazquez *et al.* have recently reported that BPO concentration has a marked effect on the setting kinetics and the ductility of cements. An optimum value of 1.5 wt % of BPO was found to yield suitable handling characteristics along with good tensile properties [17]. The range of the BPO concentrations used in the present work was from 0.7 to 2.8 wt %. Compressive strength and modulus of cured cements containing 21.4 wt % are presented in Table II. The formulation containing 1.4 wt % of BPO gave rise to maximum values of compressive strength and modulus. Vazquez *et al.* [17] observed a similar phenomenon in tensile testing for 1.5 wt % of BPO. They also showed that the higher the BPO concentration, the lower the residual monomer content (as determined by means of ^{1}H NMR spectroscopy) [17]. So, the maximal compressive properties for BPO concentrations of *ca.* 1.4 wt % would not rigorously result from an optimum value of the average molar mass of the *in situ* polymerized PMMA (as suggested by previous authors), but rather from the compromise between a low residual monomer content (for high BPO concentrations) and long chains of PMMA (for low initiator-to-monomer ratios).

Thus, in a new set of experiments, cements were formulated with this optimal BPO concentration and by varying the γ-MPS modified CR30 particles concentration (Fig. 3). No change was observed for the initial viscosity and handling properties of mixture, as compared to formulations with 0.7 wt % of BPO. On the other hand, a further improvement of compressive properties was observed, with strength and modulus values of 149 and 3375 MPa respectively in the case of 35.7 wt % of alumina concentration.

3.5. Evidence for the role of γ-MPS as coupling agent

In order to check the role of γ-MPS grafted molecules, the silanation of CR30 alumina particles was performed by using a non-polymerizable silane agent as model: 3-(acetoxypropyl)trimethoxysilane or γ-AcPS (Scheme 2). Thermogravimetry experiments led to a surface density of 8.7 μmol m^{-2}, which is a slightly higher value than for γ-MPS grafting (7.3 μmol m^{-2}). This result is consistent with the previously reported result

γ - AcPS

Scheme 2

TABLE II Compressive behavior as a function of benzoyl peroxide concentration for acrylic bone cements containing 21.4 wt % of γ–MPS modified CR30 particles and prepared with a powder-to-liquid ratio equal to *ca.* 2.5 by the mixing of $m_{\mathrm{PMMA}} = 32.1$ g, $m_{\mathrm{alumina}} = 13.9$ g, $V_{\mathrm{MMA}} = 16.9$ mL, $V_{\mathrm{BuMA}} = 2.7$ mL and $V_{\mathrm{DMT}} = 0,4$ mL

BPO concentration (wt %)	0.7	1.4	2.1	2.8
Compressive strength (MPa)*	125 (3)	133 (3)	120 (3)	122 (3)
Compressive modulus (MPa)*	2620 (140)	2820 (60)	2120 (50)	2240 (120)

*The standard deviation is given in parenthesis.

TABLE III Thermogravimetry results of radiopacifier powders extracted from acrylic bone cements containing 6.6 wt % of these particles and prepared with a powder-to-liquid ratio equal to 2.5 by the mixing of $m_{BPO} = 0.45$ g, $m_{PMMA} = 41.75$ g, $m_{alumina} = 4.3$ g, $V_{MMA} = 16.9$ mL, $V_{BuMA} = 2.7$ mL and $V_{DMT} = 0,4$ mL

Radiopacifier filler	Pristine CR30	γ-MPS modified CR30	γ-AcPS modified CR30
Loss of weight (%)	1.6	13.2*	5.0*
PMMA surface density (μmol.m^{-2})	6.2	51.2	18.8

*After deducting the loss of weight due to the initial silane molecules.

showing that the lower the non-hydrolyzable group, the higher the surface graft density [15].

Cements were prepared from these silanated particles with 0.7 wt % of BPO and for two alumina concentrations (6.6 and 21.4 wt %). Their handling characteristics were similar to those of cements based on γ-MPS modified CR30 particles in equal concentrations. Nevertheless, their compressive strengths were not improved and remained in the same order of magnitude as those obtained with pristine alumina (Fig. 3). So, the γ-MPS molecules grafted onto the alumina fillers contribute to the mechanical reinforcement of the bone cements. In order to check the copolymerization of these polymerizable groups with free MMA molecules during the setting process, alumina powders were extracted from cured cements and analyzed by thermogravimetry (Table III). Onto γ-MPS modified CR30 particles, the surface density of PMMA chains reached 51.2 μmol m^{-2} (expressed in μmol of MMA monomer units). So, large amounts of PMMA chains were grafted onto filler particles and their entanglement with free macromolecules (*in situ* polymerized or initially present in PMMA beads) contribute to a partial cross-linking of the materials.

4. Conclusions

It can be concluded that the mechanical reinforcement of acrylic bone cements is feasible by means of the previous treatment of the radiopacifier fillers surface by 3-(trimethoxysilyl)propylmethacrylate. Moreover, this route would have to reduce the production of wear particles and debris, even if wear experiments have not yet been performed. For some formulations, compressive strength and modulus reached 150 MPa and 3400 MPa respectively. Nevertheless, these formulations require high concentration of silanated alumina particles (over 35 wt %) and such cements are unprocessable due to the lack of liquid monomer for simultaneously wetting the fillers surface and dissolving the PMMA beads.

So an ideal cement would have to be prepared from a formulation combining a high amount of γ-MPS modified alumina particles, a sufficiently high quantity of PMMA beads for providing the gel effect, a BPO concentration of about 1.5 wt % and a powder-to-liquid ratio of about 2.5. Such a material could be easily handled if the steps of fillers wetting and beads dissolution could be dissociated. Thus, one route could be the use of alumina particles previously embedded in PMMA beads. The elaboration technique of such hybrid beads, the setting process and the mechanical properties of related acrylic bone cements will be reported and discussed in the next paper of the series.

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