

Properties of Acrylic Bone Cements Formulated with Bis-GMA

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Abstract: Experimental cement formulations were prepared by replacing part of the methylmethacrylate (MMA) liquid phase of a conventional surgical cement with an equivalent weight of 2,2-bis [4(2-hydroxy-3-methacryloxypropoxy) phenyl] propane (Bis-GMA), which is the reaction product of diglycidyl ether of bisphenol A and methacrylic acid. It was found that up to 50 wt % of the MMA could be replaced by Bis-GMA without reductions in flow characteristics of the precured polymers. Cements containing 20, 30, 40, and 50 wt % of Bis-GMA in the liquid component were prepared. Over this range of Bis-GMA wt %, it was found that, relative to the unmodified cement, the volumetric shrinkage (DV), the peak temperature reached during the polymerization reaction (T_p), and the flexural strength (obtained in three-point bend tests) were each significantly reduced, the flexural modulus (obtained in three-point bend tests) increased significantly, the compressive strength increased slightly, while there were no significant effects on any of the other properties determined, namely, degree of conversion of the monomer during the polymerization reaction and the glass transition temperature. The drops in DV and T_p indicate that cements whose liquid monomers are modified using Bis-GMA hold promise for use in anchoring total joint replacements. The increase in the crosslinking density with increasing amount of Bis-GMA renders the polymer matrix more brittle. This feature was considered responsible for the reduced flexural strength.

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INTRODUCTION

Poly(methyl methacrylate) (PMMA)-based bone cement is widely used in orthopedics for the fixation of joint prosthesis. However, it is well recognized that conventional bone cement is beset with a number of drawbacks such as modulus mismatch, polymerization shrinkage, and high polymerization exotherm.¹ Although the mechanical properties of modern surgical cements have been improved through improved cement preparation and delivery methods,^{2–4} polymerization shrinkage still remains a clinically significant problem. At present, all available resins for use in orthopedics undergo shrinkage due to the fact that methyl methacrylate (MMA) polymerization exhibits a 21% reduction in volume.⁵ As a result of cement shrinkage, internal stresses are developed in the cement mantle. These stresses are likely to cause microcracks and possibly gaps between the cement and bone cavity, and may be one of the factors that determines the longevity of the prosthesis.^{6,7} Furthermore, it is well known that the exothermic nature of the polymerization reaction of the

cement, together with the cement's inferior heat transfer characteristics, lead to elevated cure temperatures.⁸ High temperature observed during polymerization has been considered the main adverse effect for clinical use of bone cements.

The aim of the present work was to prepare formulations of surgical cements that are likely to exhibit smaller amounts of polymerization shrinkage and lower exotherms compared to the corresponding values for traditional formulations. For this purpose, formulations containing 2,2-bis[4(2-hydroxy-3-methacryloxypropoxy) phenyl] propane (Bis-GMA), were prepared and characterized. The molecular weight and cohesive energy density of the central part of the Bis-GMA molecule result in a relatively low volumetric shrinkage during hardening. For this reason, a traditional PMMA-based cement formulation was modified by the incorporation of Bis-GMA in an attempt to reduce the curing contraction.

Conventional surgical cements are prepared by mixing prepolymerized PMMA powder with liquid MMA monomer in a liquid-to-powder weight ratio (L/P) usually equal to 0.5. Mixing of the powder and liquid monomer constituents results in a paste or dough that can easily be placed in the prepared intramedullary bone bed. In the present work, surgical cements were prepared by replacing part of the MMA liquid by an equivalent weight of Bis-GMA monomer. The

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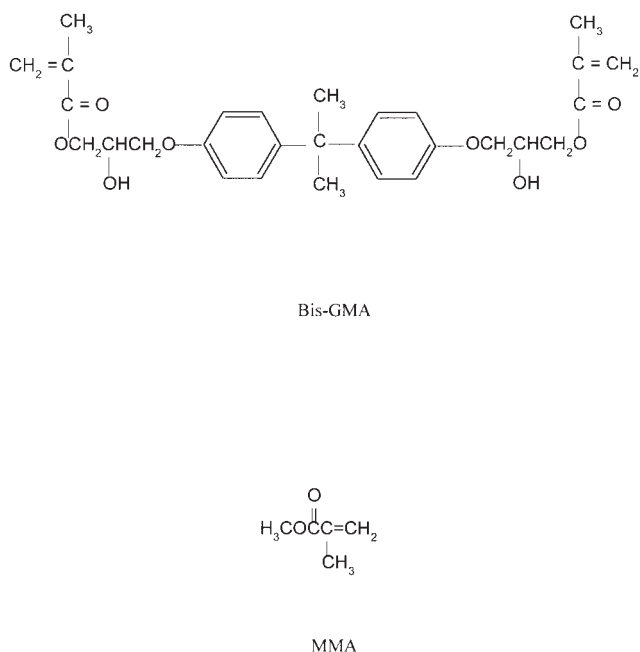


Figure 1. Chemical structure of the monomers used.

molecular size of Bis-GMA, together with the intermolecular hydrogen bonding, render this monomer viscous. The success of the implant fixation is associated with the mechanical interlock between the cancellous bone and the cement, which depends on the viscosity of the dough. In the present work, it was found that up to 50 wt % of the MMA could be replaced by Bis-GMA without reduction in workability of the precured polymers. The effect of various amounts of Bis-GMA in the liquid monomer of the cement (0, 20, 30, 40, and 50 wt %) on various properties of the cements was determined. The properties determined were the degree of monomer conversion, the glass transition temperature, the volumetric shrinkage, the peak temperature reached during the polymerization, the compressive strength, flexural strength, and flexural modulus.

MATERIALS AND METHODS

Synthesis of Bis-GMA

Chemical structure of the monomers used are shown in Figure 1. Self-curing bone cements were formulated as follows. The bisphenol A glycidyl methacrylate (Bis-GMA) resin was synthesized in our laboratory by reacting an epoxy resin, diglycidyl ether of bisphenol A (DGEBA DER 332, Dow Chemical Co., equivalent weight 174 g/eq.), with methacrylic acid (Norent Plast S.A., laboratory grade reagent) using triphenylphosphine (Fluka A.G., analytical reagent) as a catalyst. A stoichiometric ratio of 1.25/1 equivalents of acid to DGEBA, respectively, was used, together with 0.3% p/p of catalyst and 1000 ppm of hydroquinone to avoid the thermal polymerization of the vinyl groups.⁹ The reaction was carried out in a stainless steel reactor with temperature control and

nitrogen purge. The temperature was maintained at 70°C during the first hour of the reaction to avoid abrupt increments of temperature due to the high initial reaction rate, and then it was stepped to and kept at 100°C until a final conversion of 99% was reached. Excess methacrylic acid was washed out from the synthesis product with distilled water. The remaining water was extracted under vacuum at 60°C, using a Büchi rotavapor apparatus. The final product was stabilized with 500 ppm of hydroquinone. The conversion of residual acid groups was monitored by titration with an alcoholic KOH solution using phenolphthalein as an indicator; and the conversion of epoxy groups was monitored by FTIR measuring the disappearance of the 915 cm^{-1} epoxy group band, and using the 830 cm^{-1} C—H vibration band to normalize the registered spectrums.¹⁰ Figure 2 shows two interest regions of the FTIR spectrums of samples taken at different reaction times. The increment of the intensity in the 3442 cm^{-1} absorption band can be observed, which corresponds to the stretch O—H of the formed hydroxyl groups, and a reduction of the intensity of the 915 and 863 cm^{-1} epoxy group bands. In Figure 3, acid and epoxy groups conversions are compared as a function of reaction time. The epoxy group final conversion was 99%, while for the acid group it was 79% because of used stoichiometric excess. This illustrates the high order of selectivity of the esterification process. Figure 4 shows a ^1H NMR spectrum of synthesized Bis-GMA, which also contains the chemical structure and the peak assignments based in previous publications.^{9,11} The peaks at 1.94 and 1.62 ppm have similar intensities, in agreement with a high reaction conversion between epoxy groups and carboxylic acid. The number and weight average molecular weights of Bis-GMA ($M_n = 600$ g/mol, and $M_w = 630$ g/mol) were measured by exclusion chromatography using a polystyrene calibration.

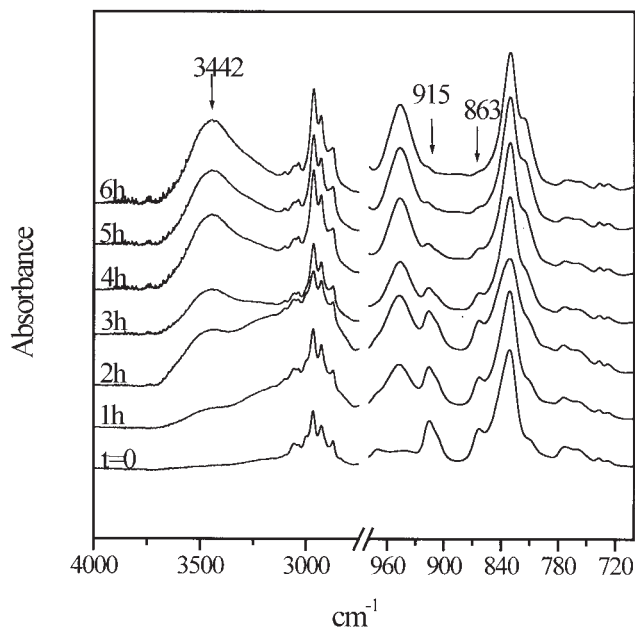


Figure 2. FTIR spectrums of samples taken at different reaction times.

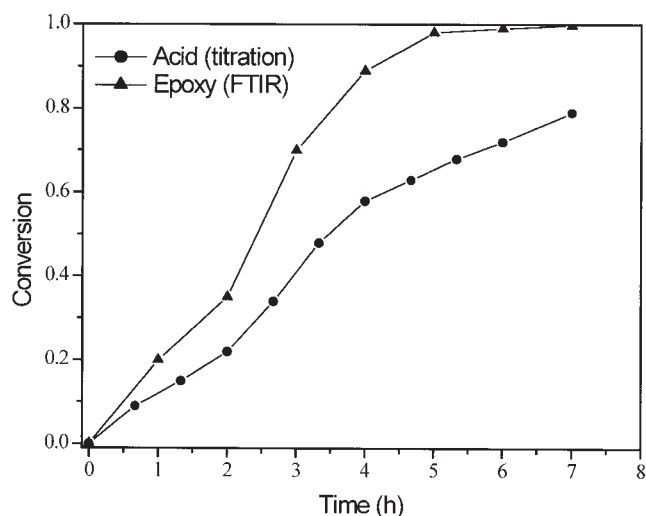


Figure 3. Acid and Epoxy groups conversions versus reaction time.

Sample Preparation

Self-curing bone cements were formulated as follows. The solid phase (*P*) was composed of PMMA powder (Subiton Laboratories SRL, Buenos Aires, Argentina) and BPO as an initiator, while the liquid phase (*L*) contained MMA, hydroquinone, and 0.24 g *N,N*-dimethyl-*p*-toluidine.

The liquid component was modified by replacing different weight fractions of the MMA monomer with an equal amount of Bis-GMA monomer. Cements containing 20, 30, 40, and 50 wt % of Bis-GMA in the liquid phase were prepared. The

designations Bis20, Bis30, Bis40, and Bis50 refer to those cements. For all the cements, *L/P* was 0.5.

Differential Scanning Calorimetry

The calorimetric measurements were made with a Shimadzu TA 50 calorimeter (Osaka, Japan), provided with software, which enables the data processing generated by each run. The calorimeter was calibrated with indium standard. The liquid-powder mixtures were prepared by hand mixing for 30 s at room temperature, in the proportion *L/P* 0.5 by weight. Samples (8–10 mg) were sealed in hermetic aluminum pans and tested immediately. Runs were carried out in the isothermal mode at 40°C under a nitrogen flow, and an empty capsule served as a reference. The variation of rate of heat output as a function of time was recorded. The sample pans were reweighed after completion of the test to determine any loss of monomer during the measurements. The measurements were carried out in triplicate.

Dynamic Mechanical Analysis

The dynamic mechanical properties were studied using a PerkinElmer DMA 7-e (Milwaukee, WI) in the three-point bending mode. The dynamic and static stresses were kept at 2×10^6 and 5×10^6 Pa, respectively. Each sample was scanned from 0 to 150°C at a heating rate of 10°C per minute. During heating the samples were subjected to strain at a frequency of 1 Hz while the probe position was recorded. The measurements were carried out in duplicate.

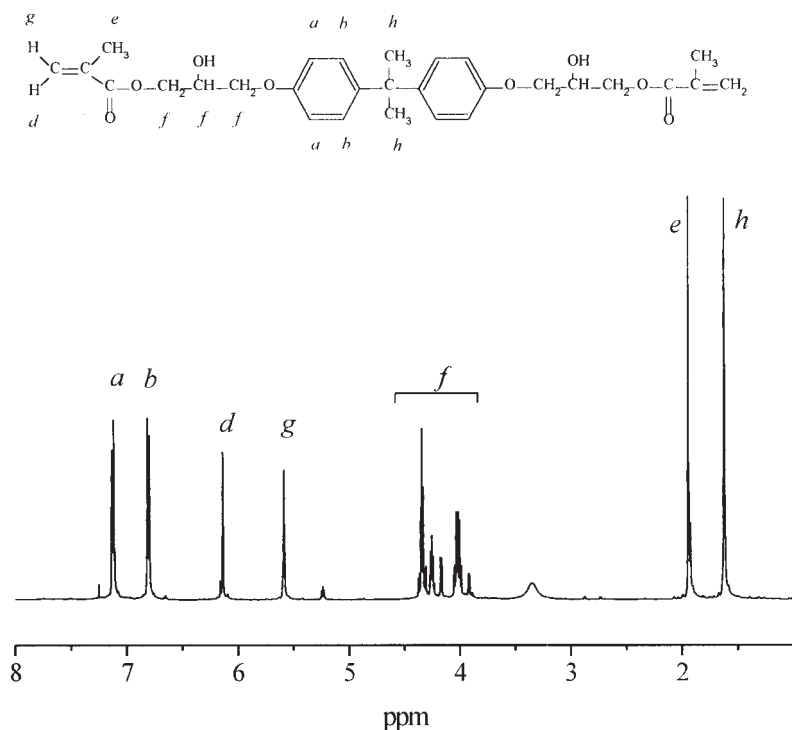


Figure 4. ^1H NMR spectrum of synthesized Bis-GMA.

Volumetric Contraction

Volumetric contraction was determined using the Archimede's principle. The density of both uncured and cured resins was measured. Uncured resins differed from cured resins in that the former were prepared using solutions of the monomers without the *N,N*-dimethyl-*p*-toluidine. Samples of about 5 g were weighed three times using a hydrostatic balance and the mean value was used as the weight of the specific specimen (m_{resin}). Subsequently, the weight of each sample was determined while it was submersed in a distilled water-filled picnometer of known volume (m_{inwater}). The temperature of the water was checked to be constant with a mercury thermometer ($\Delta T = 0.1^\circ\text{C}$). The measurements were carried out in triplicate. The difference in weight readings between m_{resin} and m_{inwater} represents the weight of water displaced by the resin (V_{water}), which was determined as follows:

$$V_{\text{water}} = \left(\frac{m_{\text{inwater}} - m_{\text{resin}}}{\rho_{\text{water}}} \right)$$

where ρ_{water} is the water density at the measured temperature. The density of the uncured and cured resins was calculated by:

$$\rho_{\text{resin}} = \left(\frac{m_{\text{resin}}}{V_{\text{water}}} \right)$$

Finally, polymerization shrinkage (ΔV) was calculated from the quotients of the two densities.

$$\Delta V = \left(\frac{1}{\rho_{\text{cured}}} - \frac{1}{\rho_{\text{uncured}}} \right)$$

Temperature Evolution During the Cure

The change in temperature during the cure of cement formulations was measured under adiabatic conditions. This condition can be achieved on highly exothermic and fast bulk polymerizing systems, as it is the case of the material studied in this work. The polymerization was carried out in an insulated cylindrical mold of 60 mm length and 40 mm internal diameter, covered with an insulated lid through which a copper-constantan thermocouple was passed and placed in the center of the mold. The temperature evolution was monitored at intervals of 3 s, and the peak temperature reached for each cement formulation was recorded. The measurements were carried out in triplicate.

Compression Testing

Compression test specimens were made by injecting the cement dough into disposable cylindrical polypropylene molds. After removal from the molds, the compression specimens were machined to reach final dimensions recommended by ISO 5833 specifications. Cylindrical compression

test specimens having an aspect ratio of 2 were deformed between metallic plates lubricated with molybdenum disulfide. True apparent stress–deformation curves were obtained by dividing the load by the original cross-sectional area and converting it into true stress assuming constant volume deformation. The deformation was calculated directly from the crosshead speed. The compressive strength was determined at the maximum load. Compression tests were carried out at room temperature ($23 \pm 2^\circ\text{C}$) in an Instron universal testing machine Model 4467 at a crosshead displacement rate of 5 mm/min. Six samples were used in each test.

Flexural Testing

Plaques for flexure specimens were obtained by casting the mixture into molds consisting of two rectangular glasses spaced by a rubber cord and held together with clamps. Test specimens were prepared by cutting slabs into beams using a diamond saw. Flexural strength and apparent flexural modulus were measured in three-point bending using specimen dimensions equal to $3.3 \pm 0.1 \text{ mm} \times 10 \pm 0.2 \text{ mm}$ cross-section and $90 \pm 5 \text{ mm}$ in length. The length between supports was equal to 60 mm. The bars were loaded to failure in three-point bending and the flexural strength (σ_f), and the flexural modulus (E) were calculated from the following standard equations:

$$\sigma_f = \frac{3FL}{2bd^2} \quad (1)$$

$$E = \frac{L^3s}{4bd^3} \quad (2)$$

where F is the load at break, b and d are the width and the thickness of the specimen, respectively, L is the length between supports, and s is the slope of the tangent to the initial straight-line portion of the load–deflection curve. The ASTM D790 standard states that results of flexural strength calculated from Eq. 1 are valid if the maximum outer-fiber strain is lower than 5%, which was verified in each test. Flexural tests were carried out at room temperature ($23 \pm 2^\circ\text{C}$) in the same machine and crosshead displacement rate used for compression tests. Fourteen samples were broken in each test.

The flexural strength was calculated from the rupture load recorded in the flexural test. The applied load versus deformation curve was fully linear over the whole range of strain, and all samples displayed maximum strain at break values lower than 5%; therefore, the flexural strength was calculated from Eq. 1. Experimental σ_f results were analyzed within the framework of Weibull statistics, which gave a good representation of the distribution of rupture loads.^{12–14} The three-parameter Weibull equation, which describes the relationship between the probability of failure and the fracture stress, σ_f , by the following relationship:

$$P_f = 1 - \exp \left[- \left(\frac{\sigma_f - \sigma_u}{\sigma_0} \right)^m \right] \quad (3)$$

P_f is the cumulative fracture probability for the stress σ_f , m is the Weibull modulus, σ_0 is a scale parameter, and σ_u is the stress below which the failure probability is zero. A common simplification that leads to a safe use of Weibull's model for brittle materials consists in taking $\sigma_u = 0$. So, the two parameter Weibull's function is obtained and Eq. 3 is reduced to

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_f}{\sigma_0}\right)^m\right] \quad (4)$$

Setting $\sigma_u = 0$ results in an overestimate of the probability of failure, which is regarded as desirable in engineering design calculations. The evaluation of the Weibull parameters, m and σ_0 , was carried out by the linear least-squares method applied to the linearized form of Eq. 4.

$$\ln\ln\left[\frac{1}{1-P_f}\right] = m\ln\sigma_f - m\ln\sigma_0 \quad (5)$$

The value of P_f for each σ_f was estimated using the following estimator¹⁵

$$P_i = \frac{i - 0.3}{N + 0.4} \quad (6)$$

where i is the rank number of the flexural strength and N is the total number of specimens tested. Experimental fracture stresses were ordered from the lowest stress to rupture to the highest and the estimator given in Eq. 6 was used to compute the fracture probability, P_f , corresponding to each value of σ_f . The data were plotted as $\ln\ln(1/1 - P_f)$ versus $\ln\sigma_f$ (Eq. 5) to calculate the Weibull parameters. Cumulative distributions of failure probability, P_f , versus σ_f were calculated from Eq. 4.

The mean value of the flexural strength is given by:

$$\bar{\sigma} = \sigma_0 \Gamma\left(1 + \frac{1}{m}\right) \quad (7)$$

and the variance is:

$$S^2 = \sigma_0^2 \left[\Gamma\left(1 + \frac{2}{m}\right) - \Gamma\left(1 + \frac{1}{m}\right)^2 \right] \quad (8)$$

where Γ is the gamma function. The standard deviation is the square root of the variance.

RESULTS AND DISCUSSION

Sample Preparation

The success of an implant fixation is associated with the mechanical interlock between the cancellous bone and the

TABLE I. Composition of the Formulations Studied

Resin	Bis-GMA (g)	Bis-GMA (mol)	Vinyl Groups
Bis0	0	0	1
Bis20	20	4	0.87
Bis30	30	7	0.80
Bis40	40	10	0.73
Bis50	50	14	0.67

The values referred to 100 g of solution Bis-GMA/MMA.

cement, which depends on the viscosity of the dough. In clinical practice, the cement must flow into the cancellous bone as pressure is applied. If the viscosity of the dough is too high, the intrusion into the bone interstitial trabeculae is poor, which prevents good mechanical coupling between bone and cement. Bis-GMA exhibits high viscosity due to intermolecular hydrogen bonding. This necessitates the use of appropriate amounts of the less viscous MMA to bring down the viscosity of the mixtures to usable levels. Table I outlines the composition of the mixes. Exploratory tests, undertaken to evaluate the maximum amount of MMA that could be replaced by Bis-GMA, showed that a maximum of 50 wt % of MMA liquid component could be replaced by Bis-GMA without reductions in flow characteristics of the paste. The molecular weight of Bis-GMA is higher than that of MMA; therefore, the number of vinyl groups per unit mass decreases with increasing proportion of Bis-GMA. All cements were prepared by mixing the liquid and powder components in a mass proportion L/P equal to 0.5.

Differential Scanning Calorimetry

The copolymerization of bifunctional methacrylate monomers leads to the formation of a crosslinked network having residual unsaturation in the form of pendant vinyl groups and unreacted monomer or oligomeric species. The presence of unreacted monomer and oligomers can have a plastizing effect (i.e., lowering the glass transition temperature) on the polymer, thereby altering the physical and mechanical properties. It is important, therefore, to assess the degree of residual unsaturation remaining after the polymerization of the formulations prepared with different MMA/Bis-GMA proportion. The end properties of dimethacrylate networks are strongly influenced by the extent of polymerization or monomer conversion. In general, the higher the conversion the greater the mechanical strength. Unfortunately, the vitrification process decelerates the reaction to a hardly perceptible rate before the completion of conversion, which leads to resins in which only part of the available double bonds are reacted. On the other hand, it has been observed that the extent of polymerization is also affected by the flexibility and the viscosity of the monomer.¹⁶ It has been speculated that diffusion of free radicals and growing polymer main chain radicals is relatively faster in less viscous systems, so comonomer systems that are more viscous are expected to result in lower extent of polymerization.

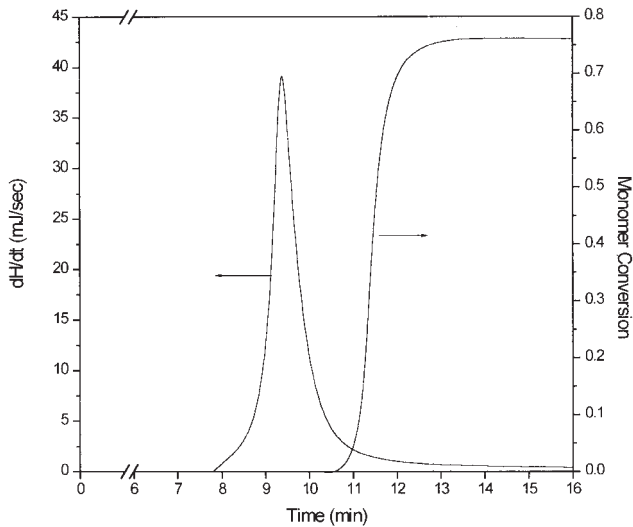


Figure 5. Typical DSC traces of reaction rate and monomer conversion versus time. The traces are slightly displaced to make the plot clearer.

The effect of the replacement of part of the MMA by the more viscous Bis-GMA on the final monomer conversion was studied by differential scanning calorimetry (DSC), which has been found to provide a useful method of monitoring the course of exothermic cure reactions.¹⁷ Because the exothermic peak due to the cure reaction is accurately detected, DSC is a suitable technique to measure the heat liberated during the polymerization of acrylic bone cements. With the assumption that the heat generated by the chemical reaction is proportional to the extent of reaction, the monomer conversion can be readily calculated. The effect of the presence of Bis-GMA on the degree of conversion was studied by curing the resins at 40°C. Figure 5 shows typical curves of reaction rate and conversion versus time. DSC measurements demonstrated that the cement formulations prepared were capable of hardening in 8 min at a temperature near body temperature. The heat of polymerization of the resin, ΔH (kJ/mol) was obtained from the area under the curve of the thermogram. The degree of monomer conversion, x , was determined using the following relationship:

$$x = \frac{\Delta H}{\Delta H_{\text{tot}}} \left(\frac{X_1}{2M_1} + \frac{X_2}{M_2} \right) \quad (9)$$

where ΔH_{tot} represents the heat of polymerization of methyl methacrylate (56.9 kJ/mol)¹⁸ and the X_i and M_i are the weight fraction and molecular weights of Bis-GMA and MMA, respectively. The factor 2 arises from the fact that Bis-GMA is a bifunctional monomer. A typical plot of x versus cure time is also shown in Figure 5. Figure 6 shows the conversion reached by monomer as a function of the Bis-GMA content. Statistical analysis showed no significant differences among the different formulations (one-way ANOVA test at the 95% confidence level). From these results, it may be concluded that, in the range of composition studied, the extent of poly-

merization of the copolymer system Bis-GMA/MMA was not affected by the proportion of each monomer.

Dynamic Mechanical Properties

DSC could not readily discern the T_g values of the resins due to the breadth of the transition region. So, the T_g was determined using a thermal mechanical analyzer (DMA). The DMA method defines a precise temperature when DSC transitions become irresolvable from the baseline, and it is approximately 1000 times more sensitive in resolving the strength of a transition than DSC.¹⁹ Moreover, DMA measures molecular motions and not heat changes as DSC. A sharp drop in modulus and probe position accompanied by a peak in $\tan \delta$ during DMA runs indicates the glass-to-rubber transition. Figure 7 shows DMA traces of probe position versus time. Only formulation Bis0, Bis40, and Bis50 are shown to make the plot more clear. An increase in the T_g produced by the presence of the Bis-GMA monomer was observed (Table II). However, statistical analysis of the T_g values showed no significant differences among the cements prepared with different amount of Bis-GMA crosslinking agent (one-way ANOVA test at the 95% confidence level).

The T_g value is a measure of chain flexibility of monomer, which depends on the nature and size of the groups of the chain. Large and polar groups, which are responsible for intra- and intermolecular interactions decrease the flexibility of the chain and increase the T_g value. Pure Bis-GMA exhibits higher T_g compared to MMA due to the presence of the rigid aromatic nuclei and mainly due to strong intermolecular hydrogen bonding in the molecule, which requires greater thermal energy to disrupt the interchain forces. As this monomer is introduced to the system, the T_g increases. On the other hand, the T_g value is influenced by the monomer conversion due to the fact that the unreacted monomer acts as a matrix

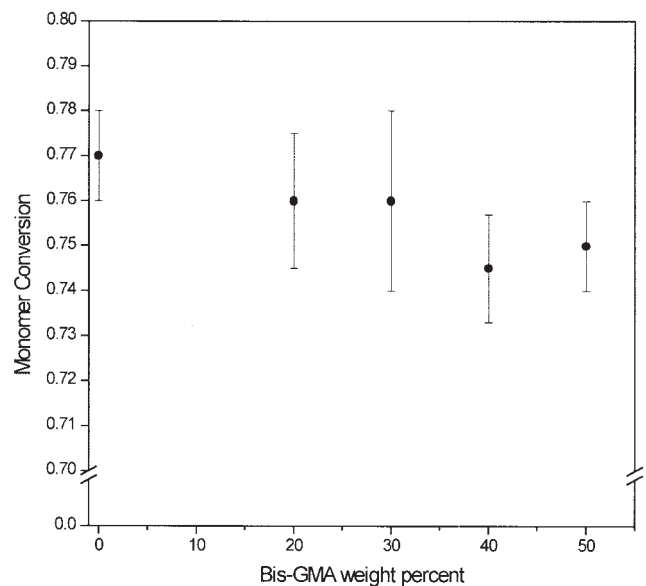


Figure 6. Monomer conversion for the formulations having different proportion of Bis-GMA.

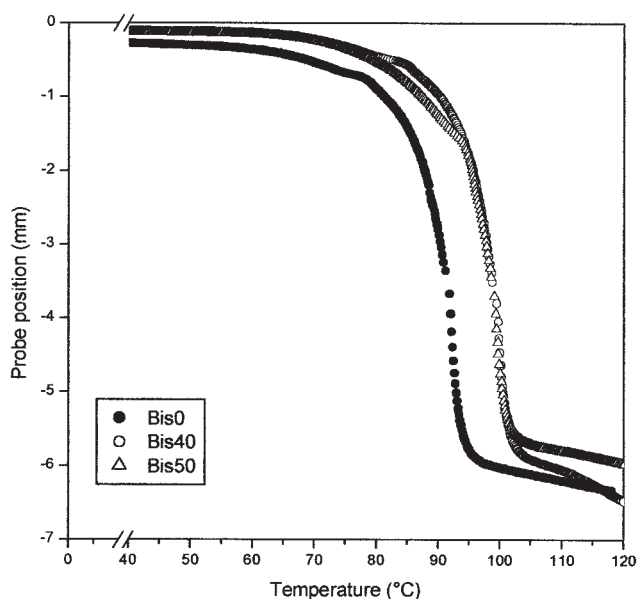


Figure 7. Typical DMA traces of probe position versus temperature.

plasticizer reducing the T_g of the cured materials. The T_g values measured by DMA measurements reveal that samples containing different amount of Bis-GMA resulted in the same T_g value, reflecting the fact that the degree of conversion is about the same.

This observation is in agreement with the results obtained by DSC.

From DSC and DMA results it may be concluded that, in the range of compositions studied, the monomer conversion and the T_g of the modified formulations are not influenced by the amount of Bis-GMA.

Peak Temperature

Table II summarizes the experimental measurements of the maximum temperature reached during the cure under adiabatic conditions. It is observed that for Bis-GMA proportions higher than 20% the peak temperature is markedly reduced compared with the unmodified cement (one-way ANOVA test at the 95% confidence level). The exothermic heat of reaction arising from the free radical polymerization of methacrylate monomers is directly proportional to the number of vinyl groups undergoing the addition reaction. Hence, the decrease in peak temperature with increasing amount of Bis-GMA is attributed to the corresponding decrease in the amount available of vinyl groups. It has been reported that, in cemented joint replacements, the high exotherm of the polymerization reaction of bone cement contributes to thermal necrosis of the tissue at the site of the implantation.²⁰ Thus, the decrease of the peak temperature observed in the formulations prepared is clinically relevant with regard to the associated thermal injury. The limit for impaired bone regeneration has been suggested to be 50°C for 1 min exposure.²⁰ Theoretical prediction of temperature evolution during hip replacement using conventional cements indicated that for

cement thickness higher than 6 mm the peak temperature at the interface bone–cement was above the limit stated for thermal injury.⁸ Hence, formulations with reduced peak temperature offer the benefit of reducing the risk of thermal injury in those circumstances in which a large volume of cement is required.

Volumetric Contraction

The conversion of the monomer molecules into polymer is accompanied by bulk contraction, which is usually denoted as curing contraction or polymerization shrinkage. Table II shows the volumetric contraction measured for the formulations containing different proportions of Bis-GMA. It is observed that the addition of Bis-GMA produced a marked decrease in the curing contraction compared with the unmodified cement. Statistical analysis (one-way ANOVA test at the 95% confidence level) indicated that the means are significantly different. The polymerization of the unmodified cement (formulation denoted as Bis0), results in substantial polymerization shrinkage because MMA polymerization is accompanied by a large volumetric contraction. The large molecular size of Bis-GMA monomer together with the presence of intramolecular hydrogen bonding gives as a result a lower cure contraction compared with MMA monomer. This feature is considered responsible of the observed decrease in volumetric contraction in formulations containing Bis-GMA.

In any cemented prosthesis, there must be no dimensional mismatch at the bone–cement interface. Perfect adaptation should be obtained while setting and maintained during mechanical cycling in function. Unfortunately, conventional acrylic bone cements do not meet this requirement due to the fact that the dimensional stability of the cement is compromised by the polymerization reaction of the matrix phase. Contraction forces result from the matrix polymerization shrinkage and cause internal stresses in the composite resin. The resultant stress may damage the bonding or cause deflection of the surrounding bone structure, and may be one of the factors that determine the longevity of the prosthesis. The formulations prepared resulted in a marked reduction in volume contraction; hence, a reduction in internal stresses in the cured resin is expected, and consequently, a decreased probability of mechanical failure.

TABLE II. Peak Temperature, Glass Transition Temperature, and Polymerization Shrinkage of the Formulations Prepared (Standard Deviations in Parentheses)

Resin	T_g (°C)	Peak Temperature (°C)	Volumetric Contraction (%)
Bis0	91 (±1)	124 (±2)	12.20 (±0.11)
Bis20	98 (±2)	122 (±2)	10.22 (±0.45)
Bis30	97 (±2)	116 (±1)	6.66 (±0.13)
Bis40	97 (±1)	106 (±1)	5.43 (±0.17)
Bis50	98 (±2)	85 (±3)	5.10 (±0.12)

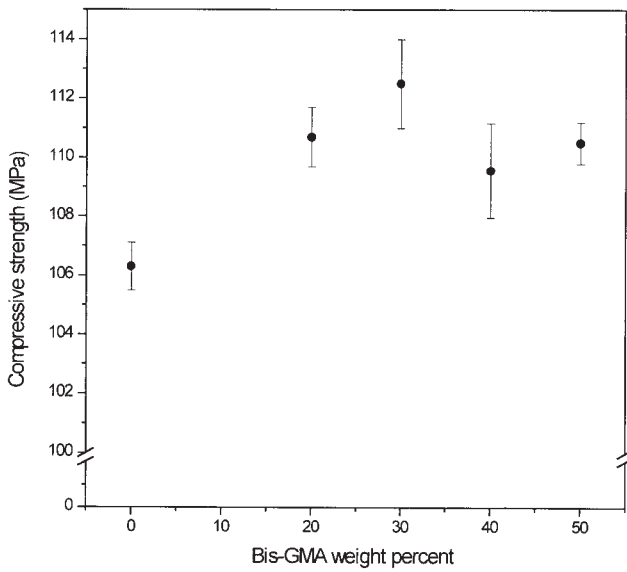


Figure 8. Influence of the Bis-GMA content on the compressive strength.

Mechanical Properties

Figure 8 shows the compressive strength for cements having different contents of Bis-GMA crosslinking agent. It can be seen that the presence of Bis-GMA increased the compressive strength (σ_y) slightly, relative to the unmodified cements. Statistical analysis carried out to compare the modified formulations (one-way ANOVA test at the 95% confidence level) showed that the σ_y values of the four modified cements are not significantly different, which indicates that the compressive behavior is not influenced by the proportion of Bis-GMA.

The international standard on flexural testing of acrylic bone cement specimens (ISO 5833) specifies the use of four-point bending; however, the flexural tests in the present work were carried out in three-point bending. The purpose of this experimental part was to study the influence of the Bis-GMA content upon the flexural strength and flexural modulus; therefore, the three-point bending mode was considered appropriate for comparative purposes. Flexural strength characterization of the cement formulations was carried out within the framework of Weibull statistics (Figures 9 and 10). A close agreement between the experimental results and the Weibull model is observed. The flexural strength values, calculated using Eqs. 7 and 8, are presented in Figure 11. As it is seen in Figure 11, the presence of Bis-GMA crosslinking agent resulted in a decrease in the flexural strength compared to the unmodified cement. Using the Mann-Whitney *U*-test at the 95% confidence level, no significant differences were found between the Bis20 formulation and the unmodified cement; however, the addition of Bis-GMA in a proportion higher than 20% resulted in a decrease in the flexural strength, which was accompanied by an increase in the data scatter. Conversely, as it is shown in Figure 12, the

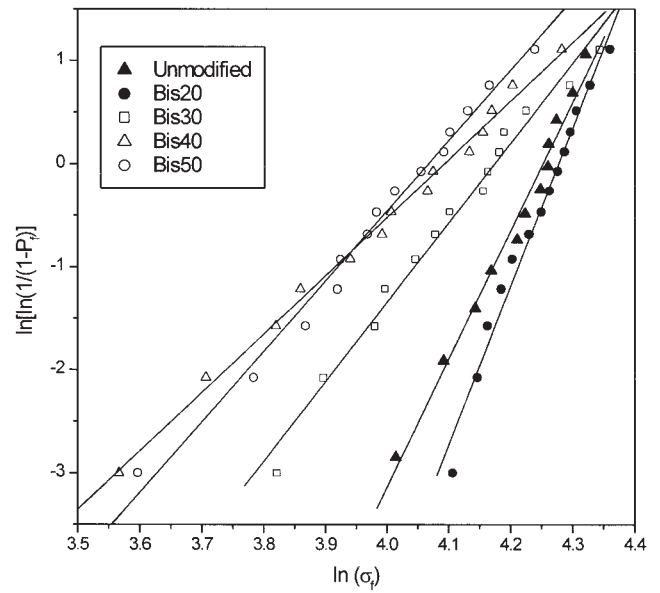


Figure 9. Weibull plots for cements prepared with 20, 30, 40, and 50% of Bis-GMA.

flexural modulus (*E*) was markedly increased by the presence of Bis-GMA. It is seen that *E* increases steadily with increasing amount of Bis-GMA crosslinked agent. Statistical analysis showed significant differences among the cements prepared with different amount of Bis-GMA (one-way ANOVA test at the 95% confidence level).

It is well known that incorporation of bifunctional monomers gives as a result crosslinked network in which the elastic modulus is increased. Thus, the results shown in Figure 12 may be explained in terms of the induction of chemical crosslinking due to the addition of bifunctional Bis-GMA

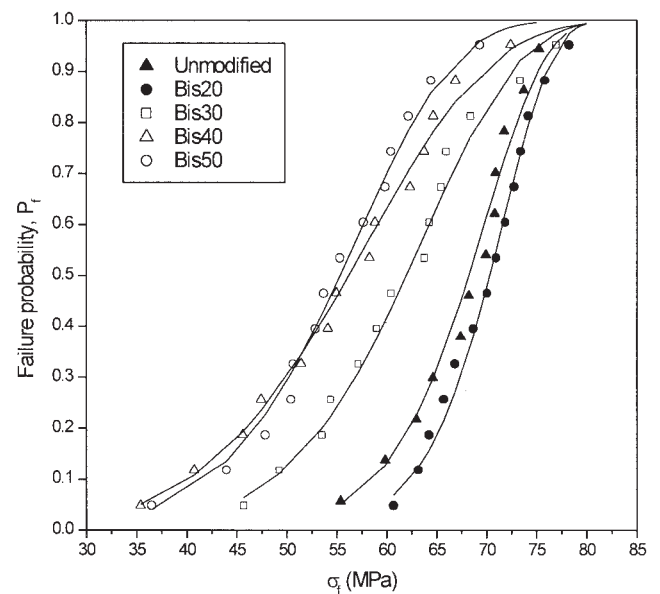


Figure 10. Weibull cumulative strength distributions for cements prepared with 20, 30, 40, and 50% of Bis-GMA.

monomer. In addition, with an increasing degree of crosslinking in a network, the polymer becomes more brittle, and hence, exhibits low resistance to fracture. Thus, the observed decrease in flexural strength is attributed to an increased crosslinking density with increasing amount of Bis-GMA, which is in agreement with results reported by previous workers.²¹

CONCLUSIONS

Experimental formulations of PMMA-based bone cements were prepared by replacing part of the MMA liquid monomer by an equivalent weight of Bis-GMA crosslinking agent without compromising the flow properties of the composite cements. The replacement of part of the MMA monomer by Bis-GMA produced no significant effect on the degree of conversion of the monomer and on the glass transition temperature. All cements displayed a marked decrease in volume contraction; consequently, the addition of Bis-GMA may result in improved clinical performance by way of decreased polymerization shrinkage and the associated stress generated at the bone–cement interface. In addition, the reduced peak temperature during polymerization offers the benefit of reducing the risk of thermal injury. The presence of Bis-GMA resulted in a slight increase in the compressive strength and a marked increase in the flexural modulus. The aforementioned improvements were not accompanied by superior flexural strength compared with the unmodified cement. The marked reduction in volume contraction and peak temperature produced by the addition of Bis-GMA encourages further research with regard to water sorption, fatigue perfor-

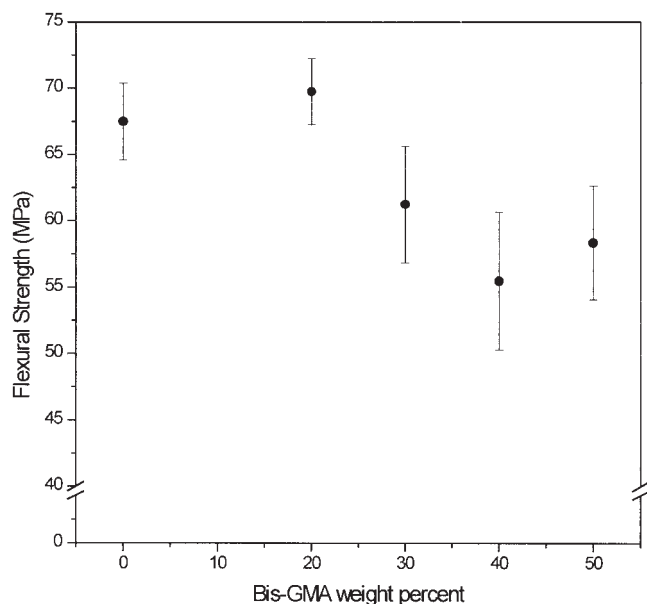


Figure 11. Influence of the Bis-GMA content on the flexural strength. Mean values and error bars were calculated using Eqs. 7 and 8, respectively.

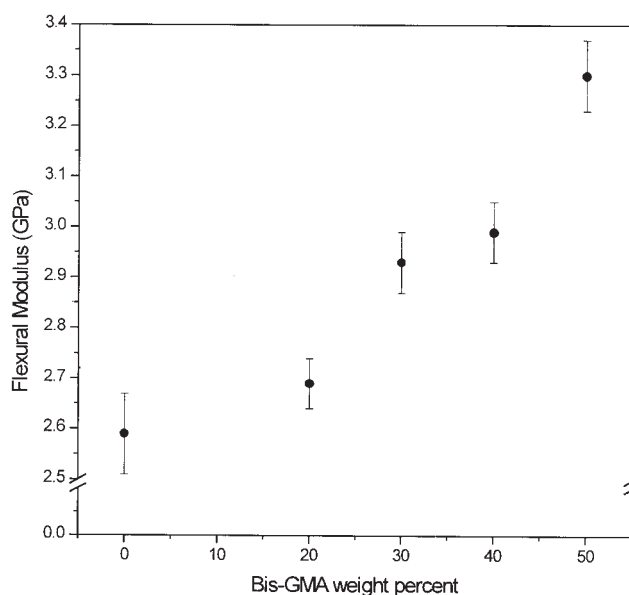


Figure 12. Influence of the Bis-GMA content on the elastic modulus.

mance, fracture toughness, creep deformation, and the addition of a viscosity modifier for Bis-GMA such as triethylene glycol-dimethacrylate. On the other hand, one of the drawbacks associated with Bis-GMA is the estrogenic potential of its precursor diglycidyl ether of bisphenol A; hence, *in vitro* tests are also required in order to identify potential toxicity.

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