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Mechanical properties of a modified acrylic bone cement with etoxytriethyleneglycol monomethacrylate

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With the aim of improving some of the disadvantages of the acrylic bone cements, an acrylic bone cement based on polymethyl methacrylate has been modified by substituting different quantities, up to 20%, of the monomer methyl methacrylate (MMA) with the same amount of ethoxytriethyleneglycol monomethacrylate (TEG). The addition of this new monomer decreased noticeably the maximum temperature and increased both setting and working times. Mechanical testing revealed that the introduction of TEG gave rise to a less fragile bone cement by increasing slightly the total deformation without any change in the rest of the tensile parameters.

1. Introduction

Bone cements have been used clinically for a number of years in orthopaedic surgery for the fixation of artificial joints with encouraging results [1]. Although various combinations of alloys, ceramics and polymers have been analysed in the past twenty years, poly(methyl methacrylate) (PMMA) has remained as an almost universal choice for bone cement. The considerable clinical success obtained with total hip replacement in elderly patients, with 90% achieving a prosthesis lifetime of 10 years or more, certainly reflects on the relative ease with which PMMA can be mixed and inserted in the femoral cavity followed by its relatively short setting time (5–15 min).

Despite this relatively good success rate of implant fixation with acrylic-based bone cement, a number of persistent problems are encountered. These disadvantages are related to the exothermic nature of polymerization and, mainly, to the relatively poor mechanical behaviour of the cement, as compared to the bone and implant performance. The local high temperature generated could produce thermal damage in the surrounding bone tissues that could also contribute to the loosening of the prosthesis. Threshold levels for thermal tissue damage (necrosis) reported in the literature range for bone temperatures as low as 48 °C to above 60 °C [2]. Although from a review of the literature no definitive answer can be given to whether bone cement produces thermal damage, the possibility of tissue necrosis cannot be ignored under certain circumstances. In addition, the main function of the cement is to serve as an interfacial phase between the high modulus metallic implant and the bone, and therefore to transfer and distribute body weight loads as well as cyclic loads due to the walking movements, from the prosthesis to the bone. Thus, the low fracture toughness of the commercial acrylic cement is one of the factors that seems to contribute to the prosthesis loosening.

Therefore, improvements in the cement properties are necessary to increase the longevity of the cement–prosthesis system. In this sense, any reduction in the exotherm and/or improvement of the fracture toughness of the commercial bone cement with retention of otherwise satisfactory properties of the bone cement would be highly desirable. There have been many attempts to reduce the temperature peak in curing bone cements by physical or chemical means [3–7]. One of the methods to reduce the polymerization temperature is to substitute, partially or completely the methyl methacrylate presently used for a methacrylate ester of long alkyl side chain [8].

As in dental acrylics, the mechanical properties of acrylic bone cements are influenced by the absorption of low molecules mass species from the environment surrounding the bone cement [9, 10, 11]. Therefore, it is to be expected that the fracture toughness of the material could be improved by the introduction of a more hydrophilic group in the bone cement.

Taking into account the above considerations, the aim of the present investigation was to examine the properties of a modified acrylic bone cement obtained by adding ethoxytriethyleneglycol monomethacrylate (TEG) to the liquid phase. This monomer forms materials which are able to retain water, as has been reported in an earlier work [12]. Setting properties, glass transition temperatures, residual monomer content and mechanical properties were determined.

2. Materials and methods

Benzoyl peroxide (BPO) (Merck) and N,N-dimethyl-4-toluidine (DMPT) (Merck) reagent grade were used as received. Commercial methyl methacrylate monomer (MMA) (Merck) containing 100 p.p.m. of monomethylether of hydroquinone was used as received. The monomer ethoxytriethyleneglycol monomethacrylate (TEG) was previously synthesized [12]. Methacryloyl chloride (Fluka), triethylamine (Merck), triethyleneglycol monoethyl ether (Fluka), and dichloromethane (Panreac) were used in the preparation of this monomer. All of them were reagent grade and used as received. The pre-polymerized beads of PMMA were supplied by Industrias Quirúrgicas de Levante (IQL) S.A. and their morphological characteristics, average molecular weight and tacticity are shown in Table I.

A typical solid/liquid ratio of 2/1 was used. The liquid component consisted of a 0.5% v/v DMPT in monomer solution in all cases. The solid component consisted of IQL beads to which the corresponding amount of finely ground BPO (1.25% w/w) was added. The liquid component was modified by the partial substitution of MMA by different amounts of TEG ranging from 5 to 20% (v/v).

The polymerization temperature was investigated by using a special cylindrical Teflon mould described in an earlier work [13] thermostatized at 37 °C. The components were mixed and the dough was packed into the plunger cavity of the mould, then, a thermocouple was positioned in the centre of the mould at the height of 3 mm in the internal cavity. The time was measured from the onset of mixing the powder with the liquid and the temperature was recorded.

Residual monomer in the cured cement was measured after an hour of polymerization at 37 °C by means of ^{1}H NMR spectroscopy [14]. NMR spectra were recorded with a VARIAN VXR-300 spectrometer operating at 300 MHz at room temperature, using mixtures of deuterated chloroform and deuterated trifluoroacetic acid as solvent and tetramethylsilane as internal reference. The glass transition temperature was determined by differential scanning calorimetry (DSC) using a PERKIN-ELMER DSC-2C instrument. The temperature range was -25–375 °C at a heating rate of 20°/min. The glass transition temperature (Tg) was taken as the midpoint of the heat capacity transition.

TABLE I Morphological characteristics, molecular weight and tacticity of the pre-polymerized beads of PMMA

Average diameter, D, µm	33.10
Interval diameter, µm	10–60
$Mn \times 10^3$	97
Mw/Mn	1.78
Tacticity (Pm)	0.26
Tg (°C)	103

The mechanical properties were determined from tensile and compressive tests carried out in an Adamel Lhomargy and an Instron electromechanic testing machine. The tensile test specimens were prepared according to the standard specification UNE-5300386, sample A, and following the ASTM-F451(86) specification in compression specimens. All test samples were aged in NaCl 0.9% solution at 37 °C for 7 days prior to the mechanical testing that was conducted on the wet specimens.

Representative fracture surfaces from the tensile specimens were analysed by scanning electron microscopy (SEM). Each specimen was cut approximately 1 cm below the fracture surface, then sputter covered with gold to render the surface electrically conducting.

3. Results and discussion

The chemical aspects of the hardening of acrylic cements are rather complex because of the swelling and partial dissolution of the PMMA particles in the MMA liquid component. It has long been recognized that the polymerization reaction when MMA is added to PMMA involves the release of 544 J/g. The amount of monomer is accurately known in these mixing systems therefore the total amount of exotherm heat can be estimated rather closely. Since the temperature and the time period during which the elevated temperature are maintained are sufficient to cause significant thermal injury to the surrounding bone, the formulation of cements which set more slowly and thus allow more time for heat dissipation may be interesting.

Fig. 1 shows the exothermic diagrams for the modified bone cement by partially substituting MMA with TEG in the liquid phase. From these diagrams we obtained the most representative curing parameters: the peak temperature, which is considered to be the maximum temperature reached during the polymerization reaction and the setting time which can be determined according to the ASTM standard (F451) as the time when the temperature of the polymerizing mass is as follows: $T_{\text{amb}} + (T_{\text{max}} - T_{\text{amb}})/2$, where T_{max} is the maximum temperature in °C and T_{amb} is the ambient temperature, 23 °C. Table II shows the values of these parameters for the modified formulations. We have found that the addition of TEG to the bone cement formulation decreased the peak temperature up to 15 °C when the cement was prepared with 20% of TEG in the liquid phase. In general, polymerization of vinyl monomers involves practically the release of almost the same heat, then the decrease in

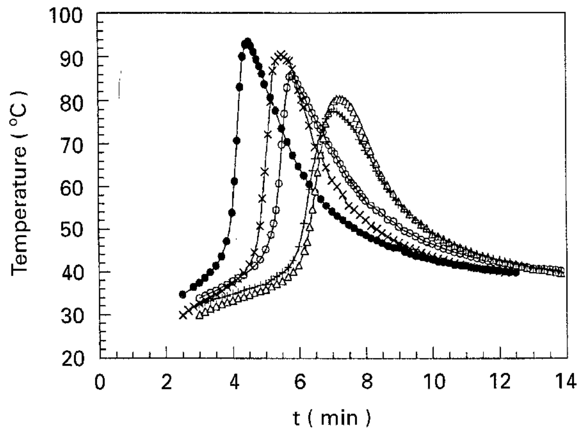

Figure 1 Changes in the evolution of temperature caused by the addition of different concentration of TEG to the formulation of bone cement: (●) PMMA, (×) 5%, (○) 10%, (△) 15%, (+) 20%.

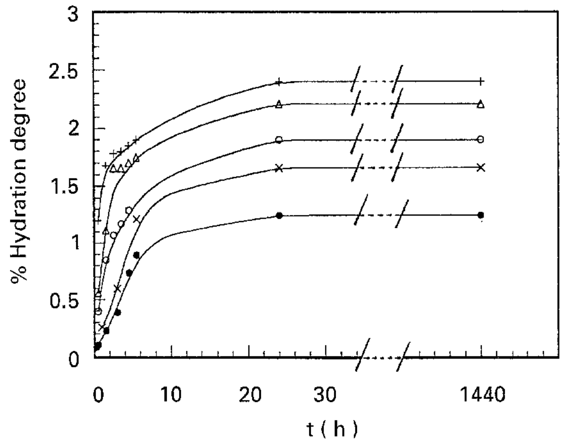

Figure 2 Variation in the time of the hydration degree of various modified bone cements: (●) PMMA, (×) 5%, (○) 10%, (△) 15%, (+) 20%.

peak temperature of the modified bone cement could be attributed to the lower polymerization rate of TE'G that allows the slower dissipation of the polymerization heat. Setting time, on the other hand, increased with increasing TEG concentration up to approximately 3 min, as was expected. This increase can be considered as favourable since it involves an increase of working time.

Table II collects also the values of *T*g obtained by DSC for the modified cements and those of residual monomer present in the cured mass obtained by means of ^{1}H NMR spectroscopy [14] after one hour of polymerization at 37 °C, according to the following expression:

$$\% \text{ Residual Monomer} = (1.5 \times A_V/A_M) \times 100$$

where A_M = average of the methoxyl integral, A_v = average of the vinyl integral, and 1.5 = a conversion factor relating the number of protons in the vinyl region (two) to those in the methoxyl group (three).

As is well known, the presence of residual monomer in the cured mass is due to the restriction in the monomer mobility towards the end of the polymerization process as a consequence of the gel effect. The point where this happens is related to *T*g of the polymer formed by the reaction. Below the *T*g the free volume of the polymer decreases substantially, restricting diffusion of monomer to the radical ends of the polymer chains. In this respect, we have found that in spite of the fact that the peak temperature decreased with increasing TEG concentration in the formulation, the values of the residual monomer present in the cured cement did not appreciably change. This can be explained by the fact that the incorporation of TEG to the formulation not only decreased the values of peak temperature but also those of *T*g, being the difference between these two temperatures of about 10 °C for any formulation. Values of residual monomer present in the set mass after one hour were about 5%, however, it has been comprobed that the residual monomer content decreased up to 3% when the samples were analysed after storing in air for a week. These values are in the range of those reported in the literature [15]. With respect to the addition of TEG to the cement we should also take into consideration that the extractability of this monomer from the onset material will be lower than that of MMA due to the greater volume of the monomeric unit. A similar behaviour has been reported in the literature for n-butyl methacrylate [16].

On the other hand, mechanical properties, were evaluated by performing compressive and tensile tests. Due to the hydrophilic character of ethyleneglycol units present in the TEG, prior to testing, the specimens were immersed in saline solution of 0.9% NaCl at 37 °C for a week in order to know the influence of water acting as a plastizicer on the mechanical properties. As we can see in Fig. 2, the swollen specimens presented a percentage equilibrium hydration degree ranging between 1.2–2.5%, this parameter being defined by the percentage of the relationship between the weight of water taken up and the weight of the wet sample at equilibrium.

TABLE II Values of peak temperature, setting time, residual monomer and glass transition temperature for acrylic bone cement modified by TEG

%TEG	*T*max (°C)	Setting time (min)	Residual mon (%)	*T*g (°C)
0	92	4.08	3.7	100
5	90	4.92	4.5	99
10	85	5.83	4.4	97
15	80	6.33	4.2	95
20	76	6.67	4.8	91

TABLE III Mechanical parameters obtained from the compression test. The standard deviation is given in brackets

%TEG	E (MPa)	σ max (MPa)
0	1767 (142)	94.85 (7.9)
5	1831 (112)	91.39 (6.5)
10	1770 (160)	86.76 (5.7)
15	1875 (111)	83.81 (5.7)
20	1850 (109)	80.05 (5.8)

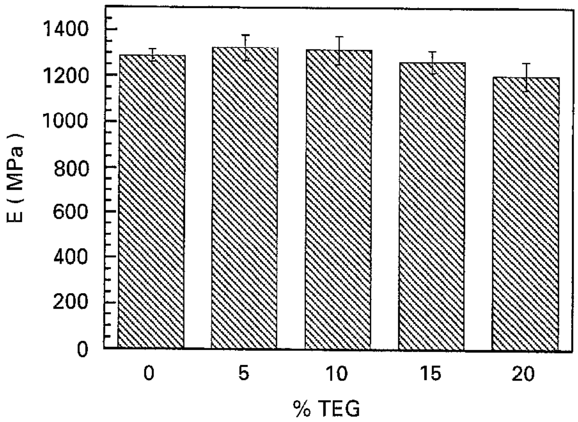

Figure 3 Variation of the Young's modulus with the percentage of TEG added as a comonomer to the liquid component.

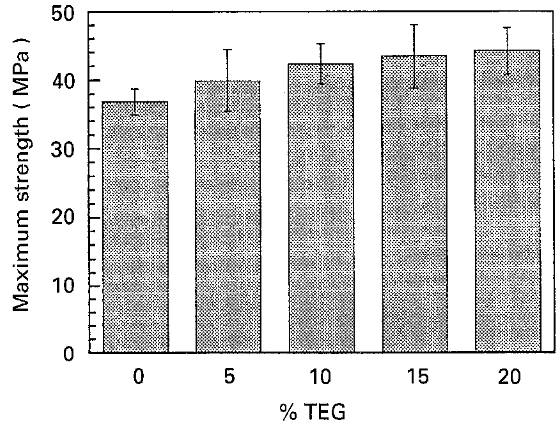

Figure 4 Variation of the maximum strength with the percentage of TEG added as a comonomer to the liquid component.

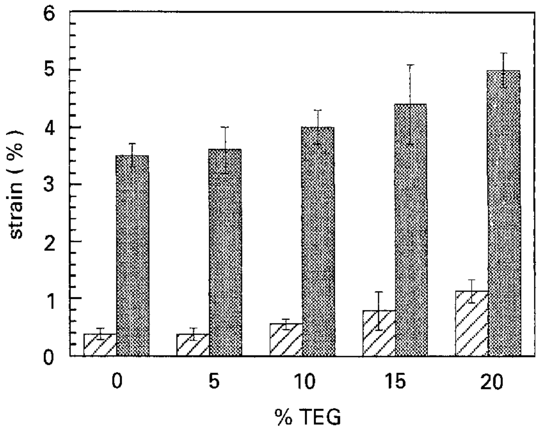

Figure 5 Variatioln of the maximum (▤) and plastic (▨) strain with the percentage of TEG added as a comonomer to the liquid component.

The compressive strength (Table III) in all the above cases is 70 MPa which is the minimum value required by the ASTM standard. On the other hand, the results of tensile test obtained for the standard bone cement and the whole series of modified bone cements with different concentration of TEG are reflected in Figs 3, 4 and 5. Young's modulus decreased slightly with increasing TEG concentration in the liquid phase (Fig. 3) whereas maximum strength increases with increasing concentration (Fig. 4). More noticeable was the variation of total and plastic strain with TEG content which increased as the hydrophilic monomer increases in the liquid phase (Fig. 5). Then, the only noticeable effect of storing samples in saline solution is to increase total strain and this increase is attributed to the plastizicing effect of the ingress of water on the cement. This means that there has been an improvement in the ductility of the modified cement.

The SEM fractographic study from the tensile fracture surfaces of a conventional bone cement and a 20% TEG modified bone cement, are illustrated in Figs 6 and 7 respectively. The fracture surface appearance can be differentiated into a smooth region, where crack initiates, and a rough region, rougher as the crack propagates further away from the origin. The smooth region includes the crack origin and represents an area of early crack growth. This region can be seen in the unmodified bone cement (Fig. 6a), and the PMMA beads can be clearly distinguished from the matrix (Fig. 6b). A characteristic typical of crazing (Mackerel or patch patterns) can be appreciated in the matrix as well as in the beads. In contrast, in the modified bone cement, the smooth region can hardly be appreciated (Fig. 7a) and a fracture surface at different cleavage planes can be seen. In this modified cement, the crazing seems to be higher in the matrix than in the beads.

Both, Figs 6a and 7a, show clearly river patterns indicating the direction of the crack propagation. However, we can easily see that this zone is larger when we test the TEG modified cement bone. In the roughest region (Figs 6c and 7c) the prepolymerized beads are not appreciated, and we can assess that the crack propagation does not distinguish between matrix and beads.

In conclusion it appears that the modified bone cement shows a less fragile fracture behaviour than the unmodified bone cement. This result confirms those obtained from the study of the tensile parameters. Thus, we can conclude that the partial substitution of MMA by TEG results in a more ductile bone cement with tougher behaviour in fracture that would probably increase the average period of service of the hip prosthesis without a new clinical intervention. Moreover, it is also important to point out that the addition of the new monomer produces an important decrease in the maximum temperature and consequently a lower tissue damage should be expected.

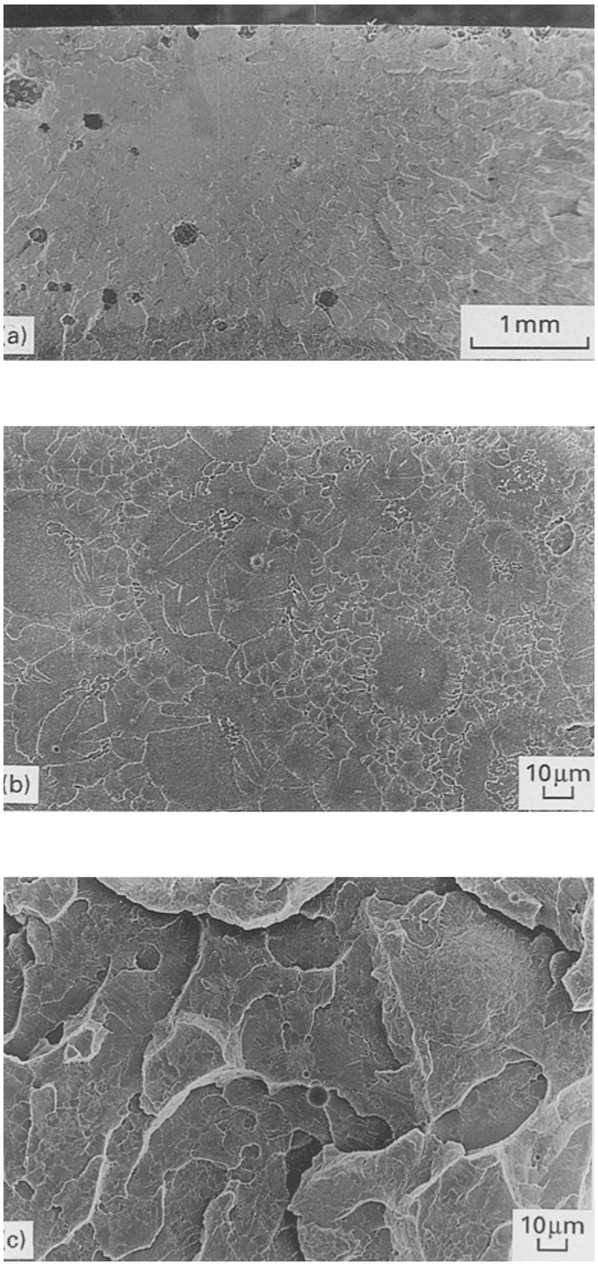

Figure 6 SEM photographs of the fracture surface, after mechanical test, of unmodified bone cement. (a) Fracture surface (× 15), (b) morphology of fracture in the smooth region. (× 365), (c), morphology of fracture in the rough region (× 365).

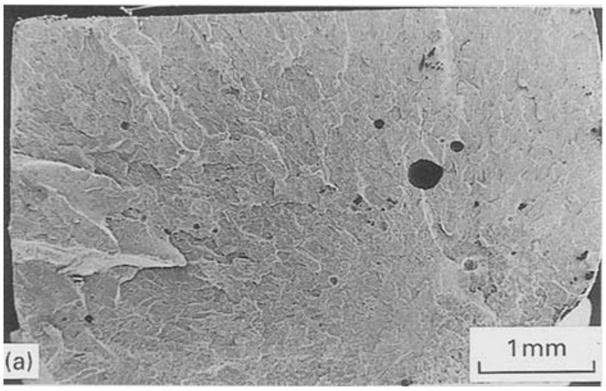

Figure 7 SEM photographs of the fracture surface, after mechanical test, of the modified cement with a 20% TEG in the liquid component. (a) Fracture surface (× 15), (b) morphology of fracture in the smooth region (× 365), (c) morphology of fracture in the rough region (× 365).

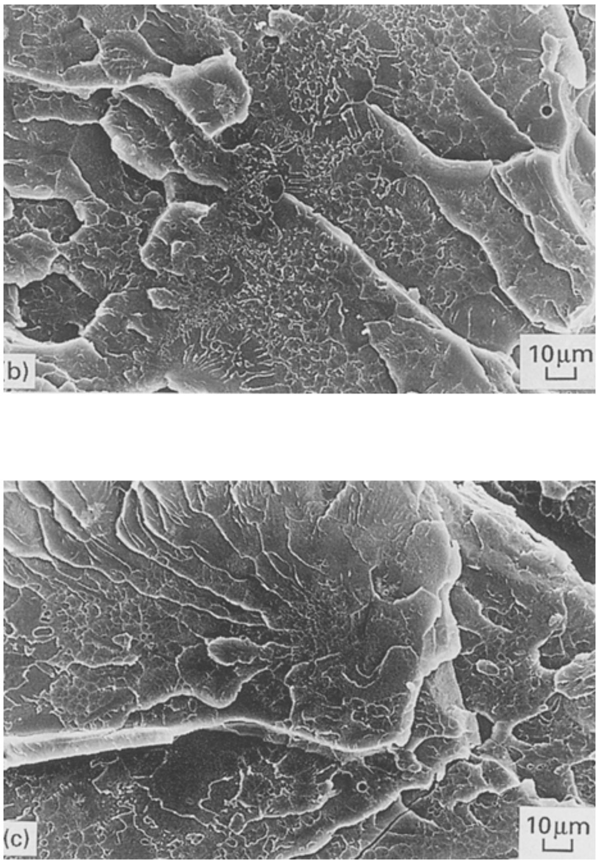

Figure 7 (Continued)

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