Influence of pressurization on flexural strength distributions of PMMA-based bone cements

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Flexural strength distributions of standard viscosity and low viscosity bone cements based on Polymethylmethacrylate were obtained by testing the materials in four-point bending according to the ISO 5833 protocol. The cement dough was poured into a mold and was allowed to cure at atmospheric pressure. An additional set of specimens of the standard viscosity cement was prepared under pressure while the cement dough was polymerizing in the mold. Following preparation, test specimens were stored in a 37 °C water bath for 48 h. The two-parameter Weibull model, which was used to analyze the data, gave a good representation of the fracture loads distribution. Low viscosity cement displayed a higher mean flexural strength and a slightly lower data scatter than standard viscosity cement. The mean flexural strength of the cement increased about 60% when pressure was applied compared with the same material cured at atmospheric pressure. The Weibull modulus, *m*, characterizes the scattering in the measured values of strength. For the cement prepared at atmospheric pressure the *m* value was 8.6 while for the cement cured under pressure it was 12.3, which reveals a reduction in the data scatter. The cement tested in four-point bending displayed lower mean flexural strength compared with the cement tested in three-point bending. The influence of the load type upon the mean flexural strength was satisfactory predicted by Weibull model.

1. Introduction

Poly(methyl methacrylate) (PMMA) based bone cement is widely used in orthopedics to fix joint replacements into the bone. The main function of the bone cement is to transfer load from the prosthesis to the bone, therefore, the effectiveness of surgical bone cement is viewed in light of its mechanical properties [1]. Currently, there are two standards and specifications for the evaluation of bone cements, the ASTM F-451 [2] and the ISO 5833 [3]. These standards specify methods for determination of compressive strength, bending modulus and bending strength of bone cements under static conditions. Clinically, the cement is cyclically loaded and would most likely fail in fatigue [4–6]. However, due to the existence of the aforementioned codes of practice, many of the mechanical characterizations have been carried out under static conditions.

Bone cement is a mixture of powder and liquid which is mixed manually before use. The mixing results in air or monomer entrapment creating pores of variable size [1, 7–14]. Further, bone cements usually contain a particulate filler providing radiopacity. Thus, the hardened material contains various defects, such as pores, voids and inclusions due to the presence of additives. The existence of flaws in a material under stress results in concentration of stresses in a manner dependent on the shape and location of the flaws. This means that the defects control the initiation of brittle fracture and their efficiencies as crack initiators are dependent on their size and shape. The random distribution of defects leads to a distribution of the measured values of strength, which explains the large data scatter observed in fracture stresses of bone cements. Therefore, the fracture characterization of bone cements should be carried out in the context of a statistical method and both their strength and strength distribution should be assessed. Such a method should include the influence of the specimen volume and the loading type on the fracture strength. A statistical model commonly used in characterization of ceramic materials is that given by Weibull [15], who proposed an empirical formula to relate the probability of failure to the fracture stress. The method can predict difference in strengths due to both different loading systems and different specimen sizes. In addition, knowledge of the Weibull distribution for a material reveals the effect of different processing parameters or subsequent treatments on the fracture behavior of the material through comparison of the Weibull distributions for the different cases.

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The aim of the following study was to analyze the capacity of the Weibull model to represent the rupture load distributions of surgical bone cements. The influence of the viscosity of the cement and pressure application upon the flexural strength distributions were evaluated. Statistical differences among the different materials were assessed by the non-parametric Mann–Whitney test.

2. Materials and methods

Flexural studies were performed on three different preparations of acrylic bone cements. Experimental formulations of standard viscosity and low viscosity cements (Subiton Laboratories, Buenos Aires, Argentina) were employed. Each dose of cement consisted of 40 g of PMMA powder and 20 g of liquid monomer. The liquid component was composed of 19.76 g MMA monomer, 0.24 g N,N-dimethyl-*p*-toluidine and 18–20 ppm hydroquinone. The solid component was composed of 36 g PMMA and 4 g $BaSO_4$ to impart radiopacity to the cement. Standard viscosity and low viscosity cements differed in the amount of benzoyl peroxide present in the powder phase.

Manual mixing in accordance with the manufacturer's recommendations was performed in a bowl for 0.5 min. The cement dough was poured into a mold and the mix was allowed to cure at atmospheric pressure. The mold consisted of two rectangular glass plaques spaced by a rubber cord and held together with clamps. An additional set of specimens of the standard viscosity cement was prepared under external pressure. The cement dough was poured into a steel mold and a pressure equal to 0.2 MPa was applied for 15 min while the cement mass was polymerizing. This pressure is equivalent to that achieved by finger packing of the femoral canal. After 15 min, samples were removed from the molds and machined to produce bars with dimensions 3.3 mm × 10 mm cross-section and 90 mm in length. The machined specimens were placed into a 37 °C water bath for 48 h as stated by the ISO 5833 protocol. The bars were loaded to failure in four-point bending and the maximum outer-fiber stresses were calculated as follows:

$$B = \frac{3Fa}{bd^2} \tag{1}$$

The standard viscosity cement prepared at atmospheric pressure was also tested in three-point bending and the flexural strength was computed by:

$$B = \frac{3FL}{2bd^2} \tag{2}$$

where B is the bending strength, F is the force at break, b and d are the width and the thickness of the specimen respectively, L is the distance between outer loading points (60 mm), and a is the distance between the inner and outer loading points in the four-point bending tests (20 mm). The samples were tested using an Instron testing machine, Model 4467, at a deflection rate of 5 mm/min.

The distribution function proposed by Weibull is the most widely used expression for characterization of brittle materials. Bone cements display a brittle behavior at room temperature, therefore, Weibull statistics were used to analyze their fracture stress distribution. The two-parameter Weibull equation, which describes the relationship between the probability of failure and the fracture stress, is given by:

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

P_f is the cumulative fracture probability for the stress σ_f, m is the Weibull modulus and σ_0 is a scale parameter. The Weibull modulus, m, is a material parameter which characterizes the scattering in the measured values of strength. The higher the m value, the less the data scatter. The mean strength is calculated from the following expression:

$$\sigma_m = \sigma_0 \Gamma\left(1 + \frac{1}{m}\right) \tag{4}$$

where Γ is the gamma function.

Different methods have been used for the evaluation of the Weibull parameters [16–20]. The most common method has been the linear least squares method applied to the linearized form of Equation 3.

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

Since the true value of P_f for each σ_f is not known, it has to be estimated. The following estimator was used in the present work, as suggested by previous workers [18].

$$P_i = \frac{i - 0.5}{N} \tag{6}$$

where i is the rank number of the flexural strength and N is the number of samples. The determination of Weibull parameters is sensitive to the number of samples tested, particularly in the range $N < 30$ specimens. Thus, when generating the Weibull parameters for a material it is necessary to use enough data points to get a good statistical representation.

3. Results and discussion

Four-point bending tests were carried out for the standard viscosity and low viscosity cements cured at atmospheric pressure and for the standard viscosity cement cured under external pressure. An additional set of specimens of the standard viscosity cement prepared at atmospheric pressure was tested in three-point bending in order to assess the influence of the load type on the flexural strength. The number of specimens of each cement tested are summarized in Table I.

The applied load vs. deformation curve was fully

TABLE I Number of specimens tested for each cement (N) prepared and tested under the selected conditions

Material	Molding	Load type	N
Low viscosity (LV)	No pressure	4PB	58
Standard viscosity (SV)	No pressure	4PB	72
	Under pressure	4PB	40
	No pressure	3PB	42

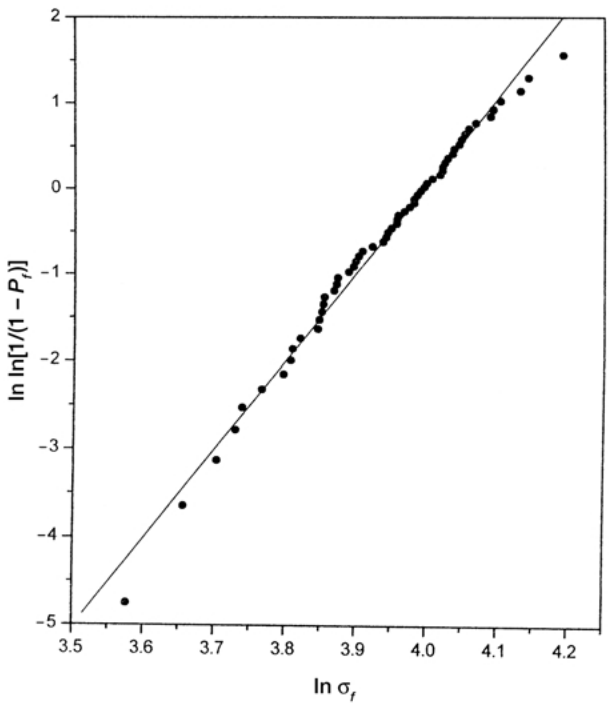

Figure 1 Weibull plot of the experimental data for the low viscosity cement prepared at atmospheric pressure and tested in four-point bending.

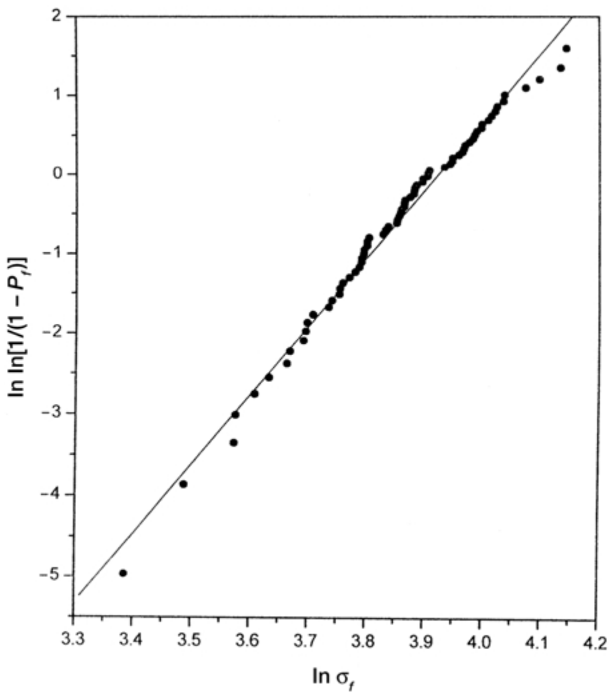

Figure 2 Weibull plot of the experimental data for the standard viscosity cement prepared at atmospheric pressure and tested in four-point bending.

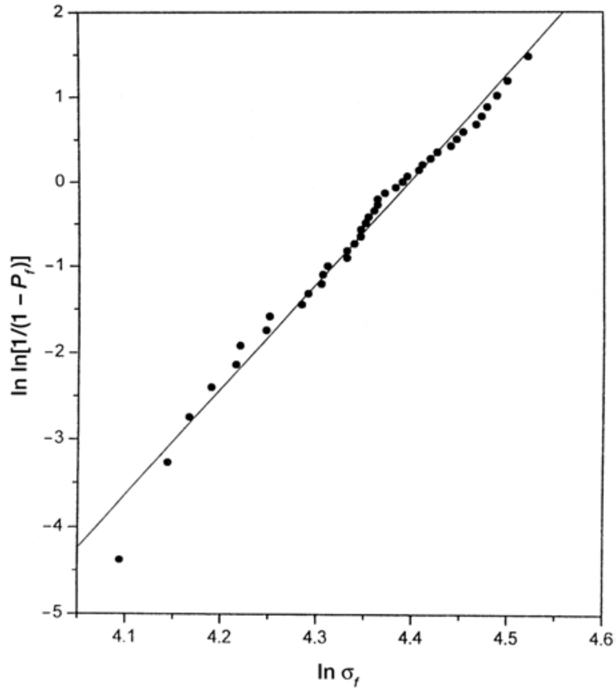

Figure 3 Weibull plot of the experimental data for the standard viscosity cement prepared under pressure and tested in four-point bending.

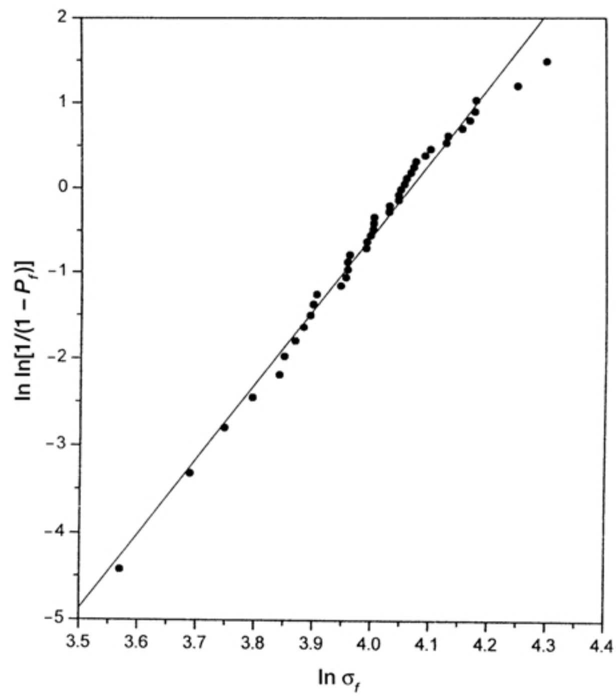

Figure 4 Weibull plot of the experimental data for the standard viscosity cement prepared at atmospheric pressure and tested in three-point bending.

linear over the whole range of strain. Fracture stresses were ordered from the lowest stress to rupture to the highest and the estimator given in Equation 6 was used to assign the fracture probability, P_f, to each fracture stress. The Weibull model was used to represent the experimental distributions of rupture stress of each test and the results for each cement are shown in Figs. 1–4. The degree of fit to the Weibull distribution was determined by how well the data group around a straight line by plotting $\ln\ln[1/(1-P_f)]$ vs. $\ln\sigma_f$ (Equation 5). Close agreement is observed between the experimental results and the Weibull model. Cumulative distributions of failure probability, P_f vs. σ_f (Equation 3), are presented in Fig. 5. Table II shows the values of the σ_0 parameter, the mean flexural strength, σ_m, Weibull modulus (m) and regression coefficients for $\ln\ln(1/1-P_f)$ vs. $\ln\sigma_f$.

The Weibull modulus values indicate a large amount of data scatter in the rupture loads, mainly because of the brittle behavior of the cement and the variable porosity of the specimens. The Mann–Whitney test comparison for

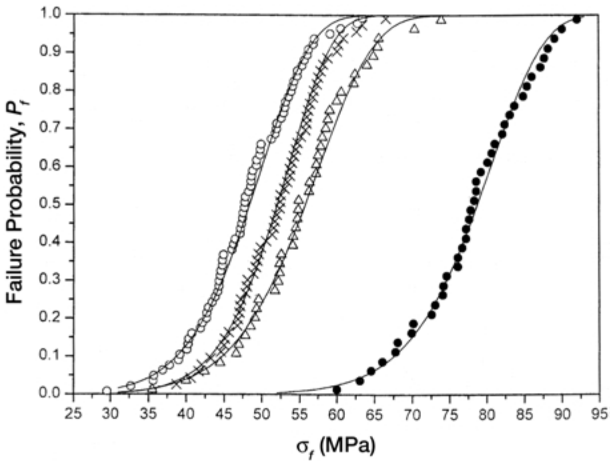

Figure 5 Weibull cumulative strength distributions for the cements presented in Figs 1–4. The solid circles are the SV cement prepared under pressure and tested in 4*PB*, the triangles are the SV cement prepared at atmospheric pressure and tested in 3*PB*, the corosses are the LV cement prepared at atmospheric pressure and tested in 4*PB* and the open circles are the SV cement prepared at atmospheric pressure and tested in 4*PB*.

the low viscosity and standard viscosity cements prepared at atmospheric pressure indicates that, at the 95% confidence level, the means are significantly different. The cause of the higher flexural strength and lower data scatter displayed by the low viscosity cement is attributed to a different porosity pattern compared with that of the standard viscosity cement. A mix having lower viscosity makes possible a more rapid and easier migration of air bubbles entrapped during mixing giving as a result a less porous material. So, the results observed are explained in terms of different porosity and pore size distribution between the cements.

Two different cements with similar flexural strength values might have very different distributions of the data points. In this case, the cement with the larger data spread would have more weak specimens and thus would probably have a greater incidence of failure. From the Weibull distribution it is possible to compare the failure probabilities at a given strength level. The comparison of the percentage of specimens broken at a certain load level demonstrates that the standard viscosity cement had a higher number of weak specimens. For example, at a load of 50 MPa, for the low viscosity cement the percentage of specimens broken was 40% while for the standard viscosity cement it was 60%. This marked difference is a consequence of both the lower flexural strength and the higher data scatter of the standard viscosity cement compared with the low viscosity cement.

It is important to consider what significance the results have from the practical point of view. Samples prepared according to the ISO protocol are cured at atmospheric pressure but it is probably more important to consider the behavior of the material cured under pressure. In an arthroplasty procedure, the cement is molded and pressurized in the intramedullary cavity. For this reason, the fracture behavior of the material prepared under pressure was assessed.

The standard viscosity cement cured under pressure displayed a mean flexural strength 60% higher compared with the same cement cured at atmospheric pressure. In addition, the data scatter was decreased by pressure application as it emerges from the comparison of the Weibull modulus of each cement. The Weibull distributions, shown in Fig. 5, reveal the magnitude of the difference in the flexural strength between the cements. At a load of 65 MPa all the specimens of the cement prepared at atmospheric pressure had broken while for the cement cured under pressure only 5% specimens failed. The results are in agreement with the fact that the porosity caused by mixing could be controlled to some extent by applying pressure on the cement dough while it was polymerizing in the mold. This observation is consistent with the results reported by previous workers. Owen *et al.* [21] found that plane strain fracture toughness, K_{IC}, increased with the fabrication pressure of the samples which controls the void content of the cement. Similarly, Freitag *et al.* [22] showed that the degree of increase in the fracture toughness produced by pressurization was dependent on the cement formulation. For the formulation studied in the present work, the pressurization of the dough resulted in a markedly increased flexural strength.

Table II shows that, neglecting experimental error, the Weibull modulus of the standard viscosity cement cured at atmospheric pressure was essentially unchanged by testing the cement in both four-point or three-point bending. This is concordant with the fact that providing a proper number of specimens is tested, the *m* value is a material property and is not dependent on how it was evaluated. On the other hand, the three-point bending tests resulted in higher flexural strength than that measured in four-point bending. All specimens prepared at atmospheric pressure were mixed, molded and stored in the same way, so, differences in the flexural tests results are solely attributed to the different loading condition. The magnitude of the difference is appreciated from the comparison of the Weibull distribution of each cement (Fig. 5). At a load of 50 MPa the percentage of specimens broken for the cement tested in three-point bending was 20% while for the cement tested in four-point bending it was 60%. An important feature of the Weibull statistics is that it predicts a loading system effect. In brittle materials, cracks of varying sizes are oriented in a random manner within the volume. The

TABLE II Scale parameter (σ_0), mean flexural strength (σ_m), Weibull modulus (m) and regression coefficient (r) in Equation 5

Material and molding	σ_0 (MPa)	σ_m (MPa)	m	r
LV no pressure 4*PB*	53.58	51.7	10.2	0.995
SV no pressure 4*PB*	49.69	47.7	8.6	0.994
SV under pressure 4*PB*	80.23	77.8	12.3	0.992
SV no pressure 3*PB*	51.17	54.9	8.7	0.992

TABLE III Influence of the load condition on the fracture strength for standard viscosity cement cured at atmospheric pressure

σ_{3PB}	σ_{4PB}	$\sigma_{3PB}/\sigma_{4PB}$ Experimental	Theoretical (Equation 7)
54.9	47.7	1.15	1.17

stress required to propagate any one of the cracks depends on its orientation with respect to the applied load and on the size of the crack. The size effect assumes great importance when components subjected to different stress states are compared. In a three-point bend test the volume of material subjected to the maximum fiber stress is very much less than that in a four-point bend specimen, which explains the results shown in Table II. For materials obeying the Weibull distribution the ratio of mean strength measured in three-point bending and four-point bending, is given by the following relationship [20]:

$$\frac{\sigma_{3PB}}{\sigma_{4PB}} = \left[\frac{(m+3)}{3}\right]^{1/m} \tag{7}$$

Table III summarizes the results obtained in three-point and four-point bending. It is observed that the experimental measurements are satisfactorily predicted from Equation (7). As it has been shown bone cements follow the Weibull distribution, so, different strengths are observed in specimens of different size or specimens tested under three-point bend or four-point bend tests. The importance of specifying the statistical parameters in reporting test results of the mechanical properties of bone cements lies in the fact that it permits comparison of studies carried out in different laboratories. In addition, knowledge of the Weibull distribution for a material, brings out the effect of different processing parameters or subsequent treatments on the fracture behavior of the material through comparison of the Weibull distributions for the different cases.

The preparation procedures for mixing and molding greatly influence the mechanical behavior of bone cements. Modification of the mixing methods of existing commercial PMMA bone cements has been the focus of much research. Centrifugation and vacuum mixing were suggested as methods to improve the mechanical properties [1, 7–9]. These improvements were attributed to the markedly reduced porosity and reduction in pore size in the hardened material. Porosity, pore size and pore-size distribution were considered the main reasons for the lower strength of surgical-grade PMMA compared with industrial grade PMMA. Given the stochastic nature of flexural strength of bone cements, it becomes clear that a statistical method should be used in order to assess the influence of different preparation techniques on its mechanical behavior. This study indicates that Weibull statistics, which is widely used in the characterization of brittle materials, gives a good representation of the rupture loads of bone cements.

4. Conclusions

Flexural strength of a bone cement was measured according to the ISO 5833 protocol. Fracture data were analyzed according to Weibull statistics, which proved to fit the flexural strength distribution of all the materials tested with regression coefficients equal to at least 0.99.

Cements tested in three-point bending resulted in a higher mean flexural strength than cement tested in four-point bending. The ratio between mean strength values measured under different loading arrangements was satisfactorily predicted by Weibull model. Knowledge of fracture load distributions for cements having different porosities gives further insight concerning to the role of the defects on the fracture behavior. The fracture mechanism of bone cements is governed by the flaws distribution and should be characterized by a statistical method.

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