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Factors affecting the mechanical and viscoelastic properties of acrylic bone cement

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The aim of this paper is to report a series of experiments investigating the factors that influence the viscoelastic properties of acrylic bone cement. The effects of the brand of cement, the length of time since mixing, temperature, the hydration of the cement, and the influence of fat and or blood in the environment on the creep and stress relaxation behavior of the cement have been studied in laboratory-prepared specimens in tension, compression and four point bending. Although there are significant differences in the viscoelastic behavior of some of the different brands of polymethylmethacrylate based cements, these differences are small by comparison with the major effects that can be exerted by the length of time since mixing and some environmental factors. These effects have important practical consequences, especially with regard to the ability of bench top and theoretical studies to predict reliably the mechanical and viscoelastic behavior of acrylic cement *in vivo*.

Introduction

A number of major reviews [1–3] have summarized the extensive literature concerning the mechanical properties of acrylic cement. Nevertheless, there remain important aspects of its mechanical behavior that have to some extent been overlooked. In particular, relatively little attention has been paid in the published literature to the influence of *in vivo* [4] (as opposed to *in vitro*) polymerization, to the influence of specimen thickness [5], both of which have significant effects on the mechanical behavior of the cement, or to the influence of a number of the factors that affect its viscoelastic behavior, exemplified by creep and stress relaxation. In the most recent review [3], e.g. the discussion of creep is limited to less than a single page of text, and stress relaxation is barely mentioned.

Creep and stress relaxation are of special significance in connection with the function of total hip replacement femoral components of force closed [6] designs (''force closed'' femoral components obtain their stability by the action of forces, as opposed to ''shape closed'' designs which obtain their stability by a match of shapes) that function on the ''taper-slip'' principle [7] and it is with these aspects of the mechanical behavior of cement that the present paper is primarily concerned. We report some experimental work on the subject and discuss the significance of the findings.

At the outset, it is important to define clearly the terms ''creep'' and ''stress relaxation'', both of which are manifestations of viscoelasticity and essentially depend upon a molecular re-arrangement [8] within the material under consideration, induced by the application of stress, and associated with flow of the mobile sections of the polymer macromolecules. Creep is defined [9] as ''the change in strain with time in a sample held at constant stress'' and stress relaxation as ''the change in stress with time in a sample held at constant strain''. Although the definition of creep implies constant load, the phenomenon also occurs with cyclic loading [10–12]. Because stress relaxation requires *time* to occur, it is affected by loading pattern, as well as by loading frequency. Unless clinically appropriate rest periods are incorporated into a loading regime that involves cycling at, say 0.5 or 1 Hz, stress relaxation in the cement may be inhibited, simply because there is insufficient time at constant strain for it to take place [13]. This is a point of major importance when comparing the viscoelastic behavior of acrylic cement *in vivo* with its behavior as reported in a number of *in vitro* and theoretical studies [14–16].

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Materials and methods

Creep and stress relaxation characteristics of various commercially available polymethylmethacrylate based bone cements and Boneloc® polybutylmethacrylate based bone cement were investigated using various techniques. Attempts were made to assess the influence of a number of variables that may be important with respect to the *in vivo* mechanical behavior of cement in total hip arthroplasty, including time since mixing (i.e. the ''age'' of the cement), the temperature of polymerization and storage, hydration and the presence of fat in the environment

Bone cement was mixed according to manufacturers instructions. Surgical Simplex®P cement was mixed by hand in the barrel of the cement syringe (Stryker Howmedica Osteonics Primary Cement Syringe no. 6205-3-000). The monomer was added to the polymer powder and stirred at 1 Hz for 2 min. Three types of specimen were fabricated:

1. *Beam-shaped specimens for bending tests* were formed by injecting cement into a simple mold at 2.5 min using a cement gun (Stryker Howmedica Osteonics Cement Gun Mark II no. 6205-1-510). Specimens were normally allowed to polymerize in the molds at room temperature (throughout this paper, room temperature is defined as 19 °C, ± 1 °C.) Cement specimens were removed from the molds at 30 min after the beginning of mixing and prepared for use by lightly finishing with 180 grit wet and dry abrasive paper, used wet.
2. *Dumb-bell-shaped specimens for tensile testing* were formed by injection of cement into simple PTFE cylindrical molds at room temperature. The cylinders of bone cement so formed were removed from the molds at 30 min after the beginning of mixing prior to machining in a CNC lathe.
3. *Cylindrical specimens for compression tests* were machined directly from molded cement cylinders.

Mixing and polymerization for all specimens took place at room temperature with the exception of those specimens that were polymerized as well as tested at body temperature. All specimens (except those tested dry, in femoral medullary contents and in Intralipid – a fat emulsion for intravenous use (Kabivitrium, Riverside Way, Uxbridge, Middlesex, UB8 2YF, England), see below) were stored in saline at 37 °C until used. CMW® cement specimens were formed and stored in the same way as described above; Palacos® specimens were formed in a similar way except that, according to the manufacturer's instructions, the polymer powder was added to the liquid monomer. The specimens were then stored as described above.

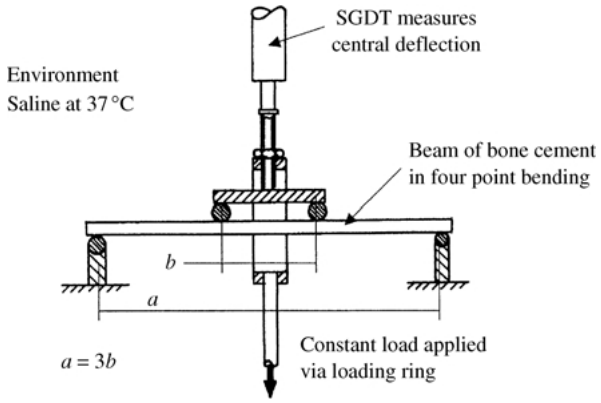

Figure 1 Four point bending creep test arrangement.

Apparatus and test protocol for assessing the creep behavior of cement

Four point bending

Creep of bone cement was measured by loading a beam specimen in four point bending under constant load (Fig. 1). The central deflection of the specimen was recorded with respect to time under load using a strain gauge linear displacement transducer model HS10, supplied by Measurements Group UK Ltd, which fed data, via a conditioning unit, into a personal computer. Specimens were 9 mm wide by 3.3 mm thick. Their length varied, being 60 mm (the ISO standard is $9 \times 3.3 \times 60\,mm^3$) for those tested dry and in saline and 75 mm for those tested in Intralipid. All specimens were prepared as described previously except that specimens tested in Intralipid were stored in Intralipid at 37 °C until required for testing. A load of 22.04 N (2.25 kg) was used to load the beams tested dry and in saline (maximum stress = 13.5 MPa) and a load of 39.2 N (4 kg) was used to load the beams tested in Intralipid (maximum stress = 30 MPa).

The test protocol for four point bending creep tests is set out in Table I.

TABLE I Testing protocol for creep in four point bending

Group	Brand of cement	No. of specimens	Polymerization temp.	Storage environment	Age at testing	Testing environment	Testing duration
1.	Simplex®P	6	37 °C	Saline 37 °C	7 days	Saline 37 °C	2 days
2.	Simplex®P	6	R.T.	Air at R.T.	7 days	Air at R.T.	2 days
3.	Simplex®P	6	R.T.	Air at 37 °C	7 days	Air at 37 °C	2 days
4.	Simplex®P	6	R.T.	Saline at R.T.	7 days	Saline at R.T.	2 days
5.	Simplex®P	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
6.	Palacos®R	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
7.	Palacos®LV40	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
8.	CMW®1	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
9.	CMW®2	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
10.	CMW®3	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
11.	Boneloc®	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	2 days
12.	Simplex®P	5 sets of 6	R.T.	Saline 37 °C	Varied*	Saline 37 °C	Varied*
13.	Simplex®P	2 sets of 5	R.T.	Intralipid 37 °C	2 or 42	Intralipid 37 °C	
14.	Simplex®P	2 sets of 4	R.T.	Intralipid 37 °C	7 or 21	Intralipid 37 °C	

*See text.

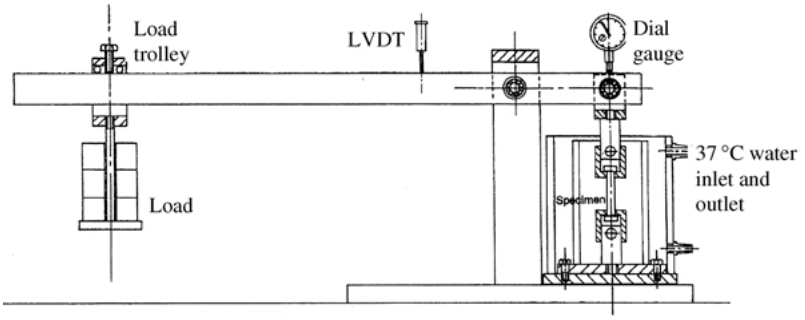

Figure 2 Tensile creep apparatus.

Tension

A special tension testing apparatus was constructed for the simple tensile and isochronous tensile creep tests (Fig. 2). The apparatus was designed so that a known tensile force could be applied along the central axis of a dumb-bell shaped specimen that was contained within a test medium (normal saline or fat) at 37 °C. The magnitude of the applied force was varied by moving the load along the loading bar and locking it in position at the required length of lever arm. For the creep tests, a constant force of 240 N was applied to the specimens, giving a tensile stress of 12.0 MPa in the gauge length. The test medium was contained within an inner tank that was surrounded by a second tank through which heated water circulated so as allow control of the temperature of the test specimen. The elongation of the specimen under load was measured by a sensitive dial gauge and by a linearly variable differential transformer (LVDT) connected to a pen recorder. The Surgical Simplex®P cement specimens were dumb-bell shaped with a 25 mm gauge length and 5.05 mm diameter (20 mm^2 cross section area) machined in a CNC lathe to fit standard grips, as used in Hounsfield Tensometer testing machines (Fig. 3). The specimens were X-rayed before testing and those with significant (i.e. larger than 1 mm diameter) voids were discarded. The specimens were stored in normal saline at room temperature, in normal saline at 37 °C, or at 37 °C in a mixture of fat and blood aspirated during primary total hip or knee replacement from several patients.

The test protocol for tensile tests is set out in Table II.

In addition to the tests outlined in Table II, in order to assess the influence of stress levels on creep, isochronous tests were performed on specimens of Surgical Simplex®P at 37 °C. The test comprised a set of short creep and recovery experiments conducted in a specific order [17]. Isochronous tensile tests were carried out on three seven-day-old specimens as follows:

A load was applied for 480 s and a trace of the extension versus time curve plotted on a pen recorder. After each load application, the specimen was unloaded and allowed to recover for 2000 s before the next, and larger, load was applied. Strain rates were calculated from the pen recorder traces for applied stress levels between 2 and 16 MPa.

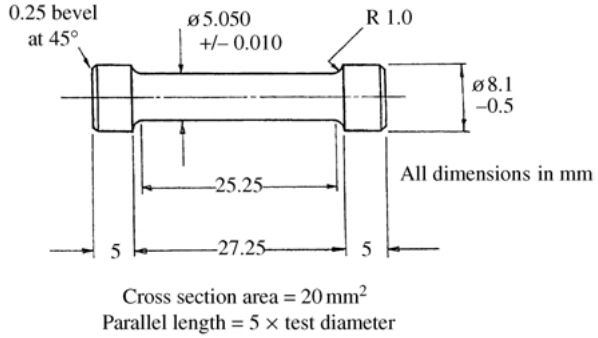

Figure 3 Tensile test specimen.

Compression

Compression tests were carried out on solid cylindrical specimens of Surgical Simplex®P bone cement, 25 mm long and 9 mm in diameter. Specimens were X-rayed before testing and those with significant voids (> 1 mm diameter) were discarded. Specimens were stored in normal saline or intramedullary fat at room temperature or 37 °C for six weeks and were tested at room temperature, 37 °C or 40 °C, Compressive strain of the specimens was measured at a load of 3 kN, giving an

TABLE II Testing protocol for creep in tension

Group	Brand of cement	No. of specimens	Polymerization temp.	Storage environment	Age at testing	Testing environment	Testing duration
1.	Simplex®P	5	37 °C	Saline at R.T.	5 days	Saline at R.T.	
2.	Simplex®P	5	R.T.	Saline 37 °C	5 days	Saline 37 °C	
3.	Simplex®P	5	R.T.	Saline 40 °C	5 days	Saline 40 °C	
4.	Simplex®P	5	R.T.	Fat and blood 37 °C	5 days	Fat and blood 37 °C	
5.	Simplex®P	5	R.T.	Fat and blood 37 °C	5 days	Fat and blood 40 °C	
6.	Simplex®P	5	R.T.	Saline 37 °C	42 days	Saline 37 °C	
7.	Simplex®P	5	R.T.	Saline 37 °C	7 days	Saline 40 °C	
8.	Simplex®P	5	R.T.	Fat and blood 37 °C	7 days	Fat and blood 37 °C	
9.	Simplex®P	5	R.T.	37 °C	7 days	Fat and blood 40 °C	

TABLE III Testing protocol for creep in compression

Group	Brand of cement	No. of specimens	Polymerization temp.	Storage environment	Age at testing (days)	Testing environment	Testing duration
1.	Simplex®P	8	37 °C	Saline at R.T.	42	Saline at R.T.	
2.	Simplex®P	8	R.T.	Saline 37 °C	42	Saline 37 °C	
3.	Simplex®P	8	R.T.	Saline 37 °C	42	Saline 40 °C	
4.	Simplex®P	8	R.T.	I.M.Fat at 37 °C	42	I.M.Fat at 37 °C	
5.	Simplex®P	8	R.T.	I.M.Fat at 37 °C	42	I.M.Fat at 40 °C	

average compressive stress in the specimens of 47 MPa. Eight specimens were tested at each data point.

The test protocol for compression tests is set out in Table III.

Apparatus and test protocol for assessing stress relaxation of cement

Four point bending

Stress relaxation of bone cement was measured using beam specimens identical to those described in the four point bending creep tests above. The four point bending stress relaxation tests were carried out in saline at 37 °C, in an apparatus designed so that a known central deformation could be applied to the specimen and maintained as time passed (Fig. 4). The tests were performed in two batches. In the first, specimens of seven different commercially available cements that had been stored in saline at 37 °C for one week following initial polymerization were tested in saline at 37 °C. In the second batch, specimens formed from Surgical Simplex®P were stored in saline at 37 °C until they were required for testing in saline at 37 °C at varying time intervals following polymerization, The force needed to keep the deformation constant as time passed was measured using a sensitive balance (Mettler Toledo PB8001) that entered the data directly into a personal computer. The maximum bending stress in the beam specimen was calculated using the recorded readings of force.

The test protocol for four point bending stress relaxation tests involved all specimens being loaded in four point bending such that the central displacement of the beam was 2.5 mm and this was held constant for the duration of the test. The detailed protocol is set out in Table IV.

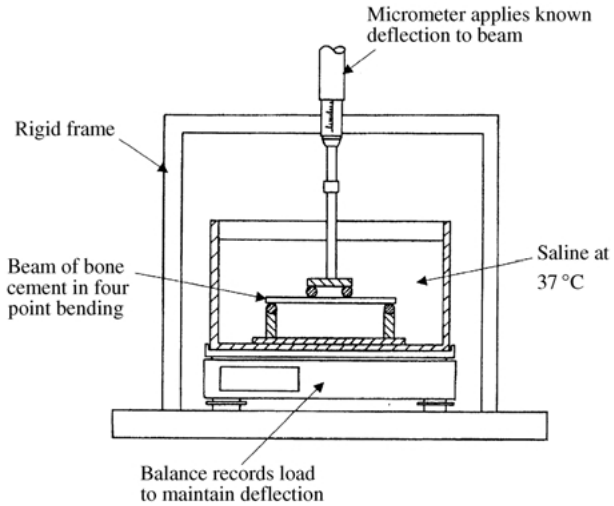

Figure 4 Stress relaxation apparatus.

Tension

Eighty millimeter long specimens of Surgical Simplex®P bone cement, of rectangular cross section 3.5 mm thick by 9 mm wide, were formed in molds as described in Section above and stored at 37 °C in saline until required for testing. They were then mounted for tensile stress relaxation tests in a Shimadzu AGS-10kND testing machine and the stress relaxation recorded using a Mintron OS-65D videoextensometer using the following procedure:

1. The load on the specimen was ramped up to 700 N (inducing a stress of 20 MPa) using a cross-head velocity of 5 mm per min.
2. Once maximum load was reached, the specimen was held at constant displacement (strain) for roughly 1 h.
3. The load on the specimen was monitored continuously during the 1 h period.

Five specimens from each batch were tested in air at room temperature after being stored in saline at 37 °C for 1, 6, 24 or 48 h. Four specimens were tested in air at room temperature after being stored in saline at 37 °C for 7 days, two specimens were tested in air at room temperature after being stored in saline at 37 °C for 14 days and three specimens were tested in air at room temperature after being stored in saline at 37 °C for 80 days.

Results

The results are depicted in the text below in graphical form. The absolute results are available from the authors if required.

Creep

Four point bending

Fig. 5 illustrates the effects of environment (wet or dry, room temperature or body temperature) on Surgical Simplex®P cement. Only the specimens from Group 1 (Table I) were polymerized and tested at body temperature. All other specimens were polymerized at room temperature and tested as set out in Table I. Both hydration and temperature have significant effects (all curves are significantly different from one another with

TABLE IV Testing protocol for stress relaxation in four point bending

Group	Brand of cement	No. of specimens	Polymerization temp.	Storage environment	Age at testing	Testing environment	Testing duration
Batch 1 – different brands of bone cement at the same time following polymerization – i.e. cements of the same ''age''							
1.	Simplex®P	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
2.	Palacos®P	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
3.	Palacos®LV40	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
4.	CMW®1	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
5.	CMW®2	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
6.	CMW®3	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
7.	Bonleoc®	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	
Batch 2 – a single brand of cement at varying times following polymerization – i.e. different ''ages'' of cement							
1.	Simplex®P	6	R.T.	Saline 37 °C	1 h	Saline 37 °C	
2.	Simplex®P	6	R.T.	Saline 37 °C	6 h	Saline 37 °C	
3.	Simplex®P	6	R.T.	Saline 37 °C	24 h	Saline 37 °C	
4.	Simplex®P	6	R.T.	Saline 37 °C	48 h	Saline 37 °C	
5.	Simplex®P	6	R.T.	Saline 37 °C	7 days	Saline 37 °C	

$p < 0.001$), with the effect of temperature being greater than the effect of dry/wet.

The results of the four point bending creep tests on various types of PMMA bone cements are depicted graphically in Fig. 6. Each test line of the figure is the average of six tests on specimens that were 7 days old at the start of the tests. All the cements that were tested exhibit creep (i.e. the central deflection of the beam increases with time when the beam is loaded with a constant load). Palacos®R creeps more than the other PMMA cements. Using the Student's *t*-test with two tails, two samples, equal variance, the difference between Palacos®R and the other cements is significant at the $p < 0.001$ level. CMW1® and CMW2® are significantly different from Surgical Simplex®P, CMW3® and Palacos®LV40 ($p < 0.001$). CMW1® is

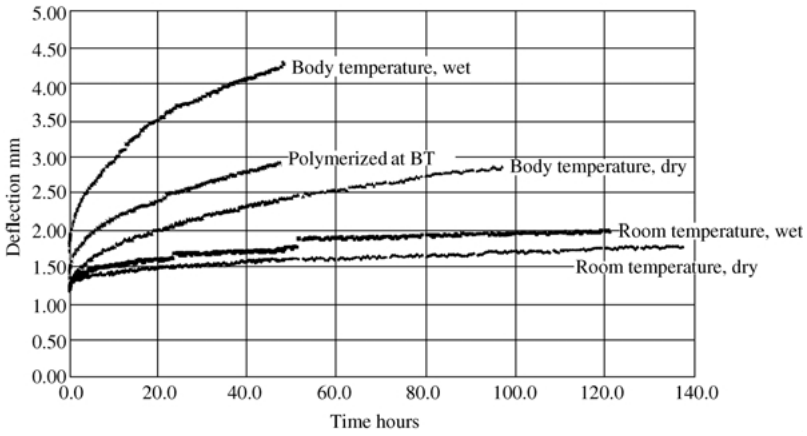

Figure 5 Creep of Simplex®P – vs. environment (wet or dry; room temperature or body temperature). Central deflection of a beam in four point bending.

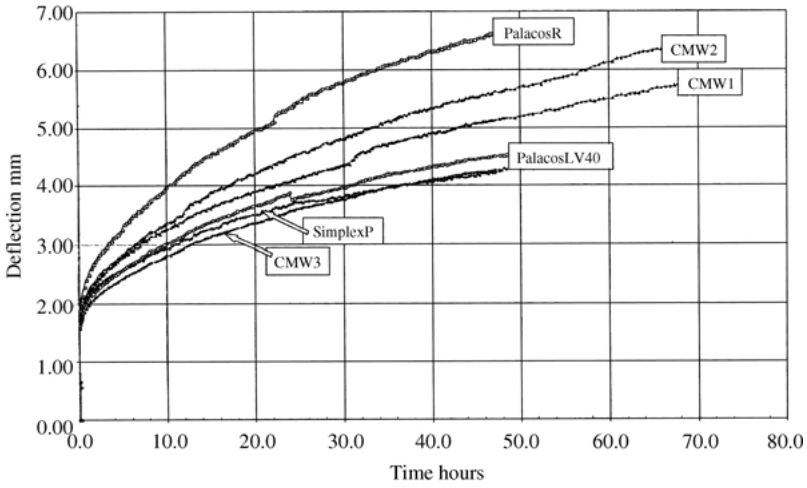

Figure 6 Creep of various bone cememnts – four point bending, specimens 7 days old at start of tests, central deflection vs. time, at body temperature.

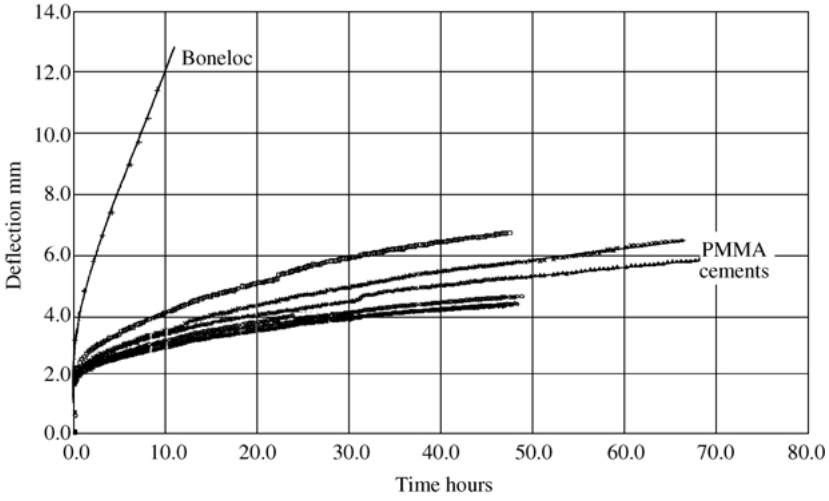

Figure 7 Creep of various bone cements – four point bending, central deflection vs. time, body temperature, including Boneloc® cement.

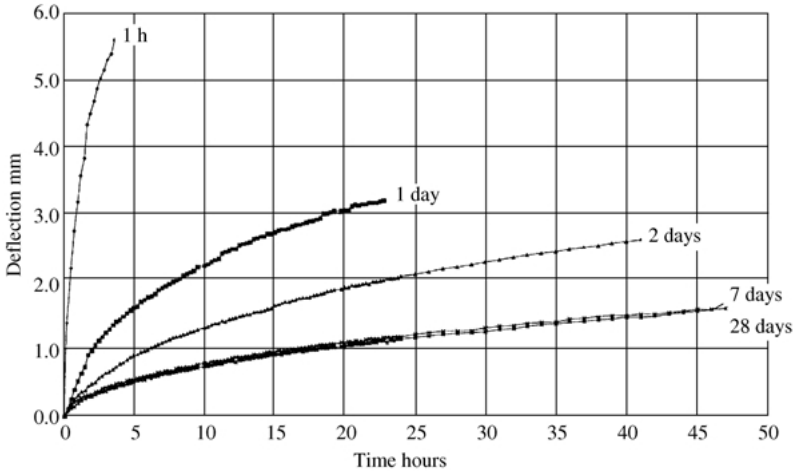

Figure 8 Creep of Simplex®P vs. age of cement – central deflection of a beam in four point bending at body temperature.

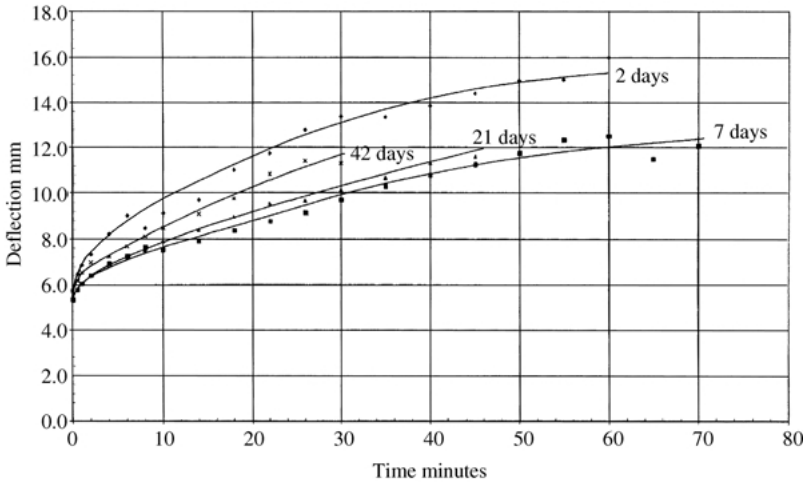

Figure 9 Simplex®P in Intralipid – four point bending, body temperature, central deflection vs. age of specimen.

not significantly different from CMW2®, nor are there any significant differences between Surgical Simplex®P, CMW3® and Palacos®LV40. Boneloc® bone cement contains significant amounts of polybutylmethacrylate, leading to a cement that has a substantially lower exotherm on polymerization. Fig. 7 re-plots the PMMA cements to a different scale and shows that Boneloc® bone cement has a significantly higher creep rate than the PMMA based cements.

The specimens reported above were all seven days old at the start of the four point bending creep tests. The influence of the age (since mixing) of the cement is summarized in Fig. 8 which demonstrates that young specimens creep very much faster than relatively old specimens. Note that the central deflections shown in Fig. 8 have been adjusted so that the deflection at time zero is shown as zero.

Fig. 9 demonstrates the remarkable effect of an

environment of fat produced by storing and testing the specimens in Intralipid at 37 °C. It is important to recognize the totally different scales of the graphs depicted in Fig. 9 by comparison with those in Figs. 5–8, especially on the abscissae. Although the maximum stresses in the cement during these bending tests were higher than in the tests depicted in Figs. 5–8, the creep rate in Intralipid is disproportionately high and is increased at all ages of cement compared to those specimens stored and tested in saline. In addition, between 2 and 7 days the creep rate decreases as expected, but at 21 and 42 days the creep rate increases.

Tension

The effects of stress level, temperature of storage and testing, and of an environment containing intramedullary fat and blood on the tensile creep behavior of cement are summarized in Figs. 10–12. The first set of tests allowed the effect of temperature on strain and strain rate to be established for specimens stored and tested in the same medium. The effect of aging of the cement was excluded by comparison of specimens of the same age at different temperatures. There was a considerable difference in both strain and strain rate at the higher temperatures (Figs. 10 and 11). Comparative results are shown in Table V that clearly demonstrates the very large plasticizing effect of an environment of intramedullary fat, an effect in tensile creep similar to that of an artificial fat environment (Fig. 9) on creep in four point bending.

The second set of tests, the isochronous tensile tests, showed the effect of varying stress level on creep rates for specimens stored and tested in saline at 37 °C for seven days before testing (Fig. 12).

Compression

The effects of temperature and fat in the environment on compression creep are summarized in Table VI(a) and (b), and are essentially similar to their effects on creep in four point bending and tension. Increasing the temperature increases strain. The effect of the uptake of intramedullary fat into the specimens is to increase the

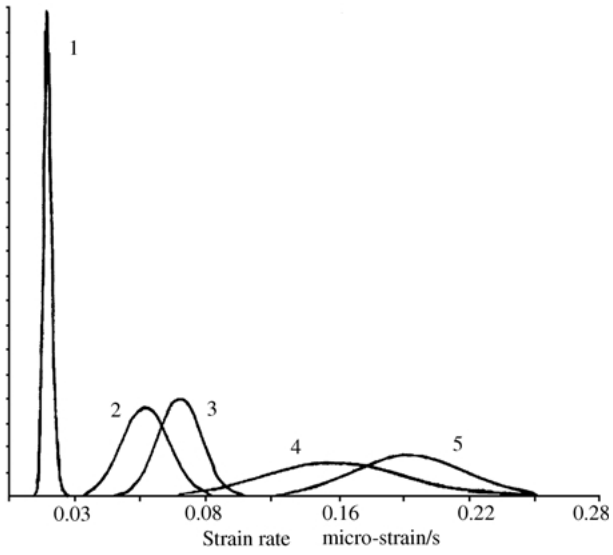

Figure 10 Normal distribution of strain rates of 5-day-old specimens: (1) in normal saline at room temperature, (2) in normal saline at 37 °C, (3) in normal saline at 40 °C, (4) in fat at 37 °C and (5) in fat at 40 °C.

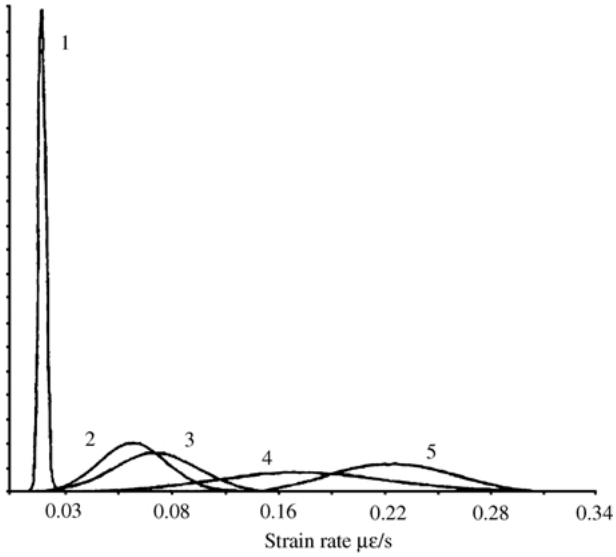

Figure 11 Normal distribution of strain rates of 6-week-old specimens: (1) in normal saline at room temperature, (2) in normal saline at 37 °C, (3) in normal saline at 40 °C, (4) in fat at 37 °C and (5) in fat at 40 °C.

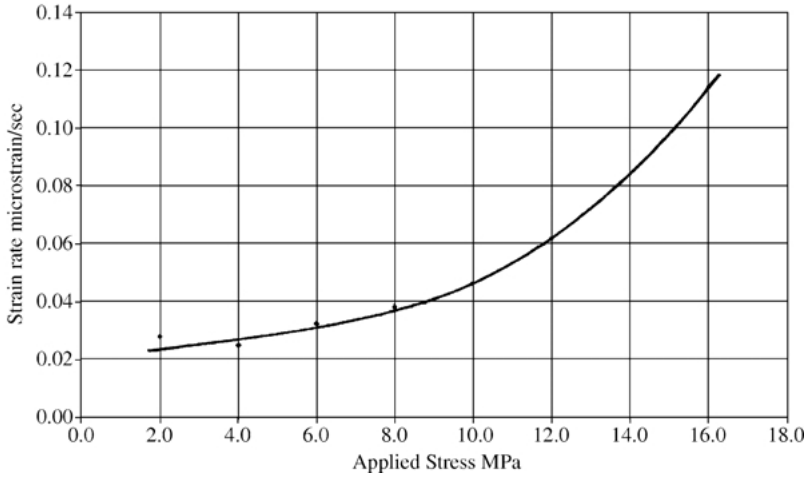

Figure 12 Isochronous stress/strain rate of Simplex®P, tensile stress in saline at body temperature.

TABLE V Creep in tension – effect of environment (including temperature) and age on strain rates – Simplex P cements (test conditions in Table II)

Time	Environment	Temperature (°C)		Environment	Temperature (°C)	Ratio of strain rates	Significance
5 days	Fat	37	Compared with	NaCl	37	= 2.37	$p < 0.001$
5 days	Fat	40	Compared with	NaCl	40	= 2.34	$p < 0.001$
6 weeks	Fat	37	Compared with	NaCl	37	= 2.38	$p < 0.001$
6 weeks	Fat	40	Compared with	NaCl	40	= 2.52	$p < 0.001$

TABLE VI Creep in compression – effect of temperature on strain at 47 MPa

	Ratio: first to second variable	Significance
(a) Simplex P		
Normal saline: 37 °C vs. RT	1.91	$p < 0.0001$
Normal saline: 40 °C vs. 37 °C	1.41	$p < 0.01$
Intramedullary fat: 40 °C vs. 37 °C	1.25	$p < 0.002$
(b) Simplex®P		
Fat at 37 °C vs. saline at 37 °C	1.37	$p < 0.001$
Fat at 40 °C vs. saline at 40 °C	1.21	$p < 0.02$

strain, so increasing the rate and amount of creep at a given stress.

Stress relaxation

Four point bending

The results of the first batch of tests, comparing stress relaxation characteristics of six different commercially available bone cements stored for 7 days in saline and tested in saline at 37 °C, are summarized in Figs. 13 and 14. Fig. 13 shows the stress relaxation of Palacos®R bone cement. Six tests are plotted on the graph, which is typical of all individual bone cement test results, and shows that the stress relaxation characteristic is reproducible (results are not statistically significantly different at the $p = 0.001$ level). The results for the six different commercially available bone cements are shown on Fig. 14, each line being the average of six tests. This figure shows that all bone cements exhibit stress relaxation under conditions of constant strain, in a similar way to the results of the creep tests in four point bending. Stress relaxation of Palacos®R and Surgical Simplex®P is not statistically significantly different at the $p = 0.001$ level, but both cements are significantly different from all others tested. The CMW cements are not different from each other, but are different from Palacos®LV40, all at the $p = 0.001$ level.

The results from the second batch of tests, comparing stress relaxation in specimens of a single brand of cement of different ages are given in Fig. 15. The results are from four point bending stress relaxation tests where the bending specimen was given a fixed central displacement and the load needed to maintain that displacement monitored. The effect of time since polymerization (i.e. the ''age'' of the cement) is marked.

Tension

Fig. 16 shows stress relaxation results from tension tests on rectangular cross-section tensile specimens stored in saline at 37 °C until they were removed for testing at 7 days, the tests themselves being carried out at in air at room temperature. Again, the effect of the time since mixing is striking.

Further information on the effects of age, i.e. the time since mixing, on the stress relaxation of cement under tension is shown in Table VII for periods of 180 and 3600 s of constant strain. The figures are given as a percentage reduction of the stress value at the start of the relaxation test and show very clearly the increased rate of tensile stress relaxation the ''younger'' the cement is at the time of testing. Even at 80 days following mixing, tensile stress relaxation is still significant.

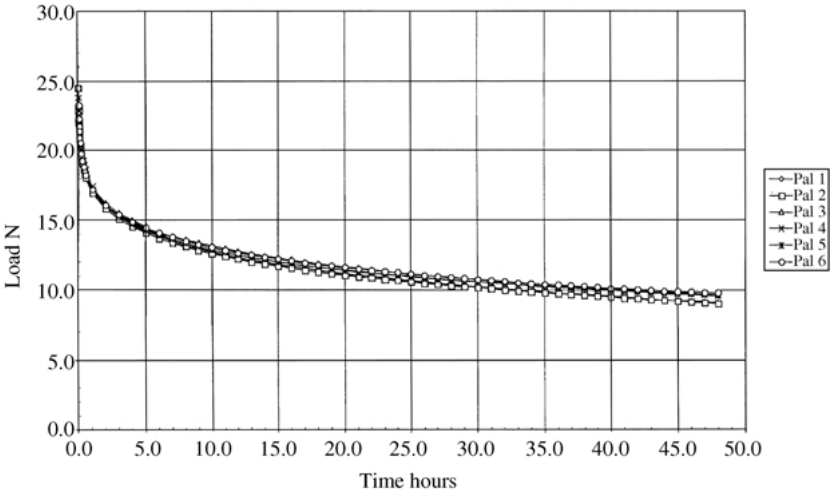

Figure 13 Stress relaxation of Palacos®R, four point bending, constant central deflection, specimens 7 days old at start of tests, in saline at body temperature.

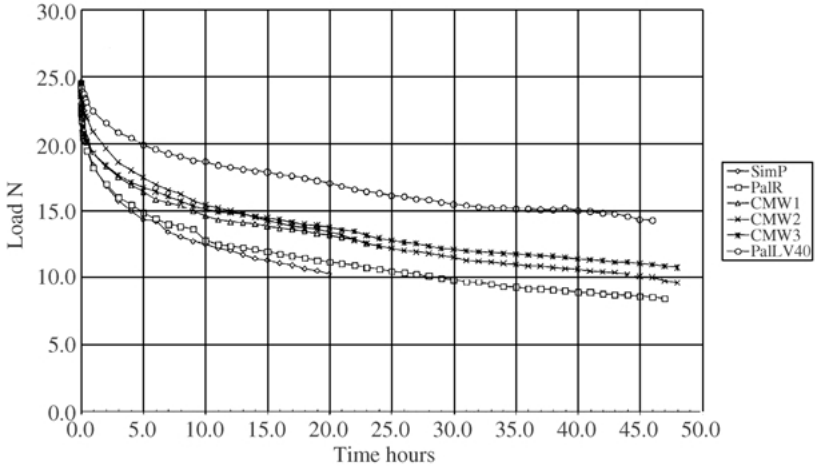

Figure 14 Stress relaxation of various bone cements; four point bending, constant central deflection in saline at body temperature, specimens 7 days old at start of tests.

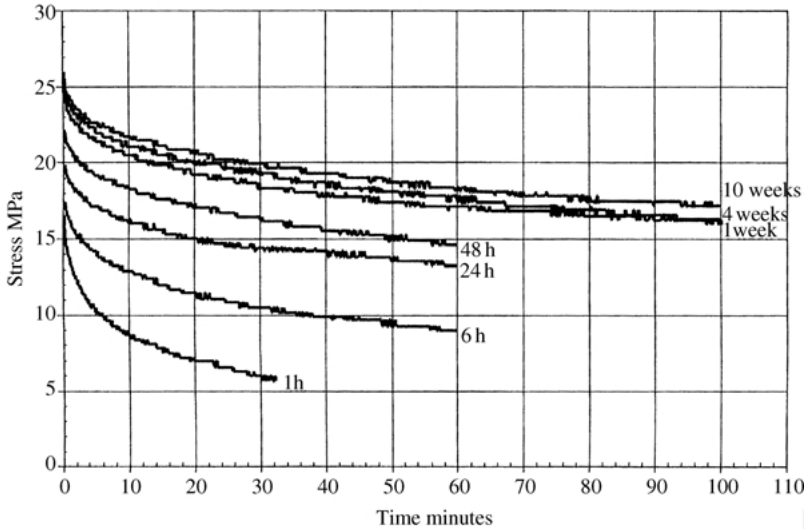

Figure 15 Stress relaxation, Simplex®P, four point bending, body temperature vs. age of specimen.

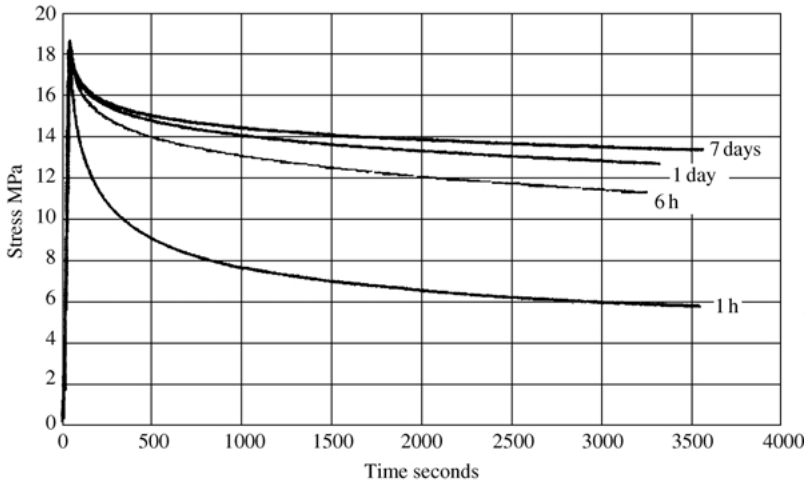

Figure 16 Tensile stress relaxation, Simplex®P, room temperature, air vs. time.

Discussion

The results set out above and in the tables show that while there are differences between the viscoelastic behavior of the various brands of polymethylmethacrylate based cements, these differences are substantially less than the effects of a number of potentially important environmental factors on the viscoelastic behavior of these cements, particularly if more than one of these factors are acting together. Where a full range of commercially available PMMA cements were not tested, Simplex®P was used as a ''typical'' cement.

By contrast, the only polybutylmethacrylate cement

TABLE VII Reduction in stress due to stress relaxation at 180 and 3600 s after start of test for specimens of various ages at the start of the tests

Specimen age	σ_{180} (%)	σ_{3600}(%)
1 h	40	70
6 h	23	44
24 h	21	37
48 h	21	37
7 days	20	34
14 days	19	32
80 days	19	30

that was tested (Bonleoc® – that has a glass transition temperature of about 55 °C [18]) was found to have viscoelastic properties that are very much more marked those of the polymethylmethacrylate based cements. There has been little clinical experience with butylmethacrylate containing cements other than the generally catastrophic results with Boneloc® [18–24], though to date, the use of London Hospital cement (also a butylmethacrylate containing cement [25]) in a limited number of patients at the London Hospital has been satisfactory [25], and experimentally, in sheep, improved results have been reported with its use in hip arthroplasty [26]. Interestingly, the only femoral component to have survived satisfactorily at 5 years with the use of Bonleoc® [27, 28] is a ''forced closed'' [6] design (the polished Exeter) that functions on the ''taper slip'' [7] principle in which the viscoelastic behavior of cement is believed to play an important part in the way in which stems of such design function [29, 30]

Whether the viscoelastic properties of the polymethylmethacrylate based cements are examined by measuring creep or stress relaxation in either four-bending, tension or compression, the factors influencing these properties are shown to be the same and fall into the following groups:

1. *The ''age'' of the cement* (i.e. the time interval between mixing and testing) when tested probably exerts its effect (Figs. 8, 15 and 16) through the gradual reduction of monomer by further polymerization with time following initial polymerization (set time) – i.e. aftercure. The monomer acts as a plasticizer and this action becomes less with time as the monomer content becomes less. For example, creep rates at 1 h or 1 day after forming the cement are substantially higher than at 1 week or 4 weeks (Fig. 8, deflection at 20 h for 1 day specimen is about 2.8 × deflection at 20 h for 4 week specimen). As the degree of polymerization increases, so the molecular weight and chain interactions increase.

2. *Environment*: Hydration of the cement has a relatively small, but nevertheless consistent, effect on increasing its viscoelastic behavior (Fig. 5), first reported in 1990 [10], unlike the effects of an environment containing fat (Figs. 9–11), that are marked, whether the fat is synthetic or derived from the medullary canal of the femur. When the effect of testing at body temperature (Fig. 5), as opposed to room temperature, is added to that of fat, the increased viscoelastic behavior of the cement is substantial. The mechanism through which the effects of hydration and of fat are mediated is uncertain, but they probably act as plasticizers in the same way as residual monomer. Figs. 8, 15 and 16 demonstrate the effect of a gradually diminishing level of residual monomer with time following polymerization, due to ''aftercure'' [31], a process that continues for years.

There is an interesting interaction between the effects of the ''age'' of the cement and the effects of a fatty environment: specimens stored and tested in an artificial fat emulsion such as Intralipid, show that the effect of the passage of time (which reduces creep rate) is overwhelmed by what is probably the plasticizing effect of the fat on the cement and that the creep rate thus becomes faster at 6 weeks than at 1 week (Fig. 9). When the environment is changed to one of human intramedullary fat and blood recovered at primary hip arthroplasty, the effects are similar. Tension tests show that creep rates in intramedullary fat are about 2.4 × the creep rate in saline, a finding that is significant ($p < 0.001$).

3. *Temperature*: the properties of a thermoplastic polymer such as bone cement change as the temperature of the environment changes. At temperatures below 0 °C, bone cement behaves as a brittle material, i.e. it will deform elastically and fail with very little plastic deformation. As the temperature rises, so the viscoelastic properties of the polymer become more important, until, at the glass transition temperature (about 95 °C for PMMA bone cement) the polymer becomes ''leathery'' [32]. Bone cement in the body functions at 37 °C, or slightly higher [33], so it is important to determine its characteristics at this temperature (Fig. 5). Figs. 10 and 11 show that the strain rate of bone cement at 37 and 40 °C is significantly higher than at room temperature, for both five-day-old and six-weeks-old specimens (strain rates were 3.55 times higher and 4.43 times higher at 37 and 40 °C ($p < 0.001$) than for specimens tested at room temperature). The shape of the distribution curves is also interesting – they show that the strain rate measured at room temperature is well determined and confined to a narrow band of values. However, the curves show that the strain rate values in saline at 37 and 40 °C are less well defined (curves are spread wider, therefore a larger range of values) and that the strain rates in intramedullary fat are even more widely spread. Consequently, in bone cement under load, a range of creep strain rates will be found that will change according to the temperature and environment.

Further clarification of the basis for the effects of temperature change on the mechanical and viscoelastic behavior of acrylic cement will require some type of structural study, using either dynamic mechanical thermal analysis [34], differential scanning calorimetry [34] or mass spectrometry. Such work is beyond the scope of the present paper.

4. *Stress level*: in common with all conventional materials, the higher the stress, the higher the creep rate. Most of the tests reported in this paper were carried out at stress levels which ensured that relatively large amounts of creep occurred in relatively short times in order that the experiments were manageable. Fig. 12 shows that the

creep rates at the low stress levels (approximately 2–8 MPa) likely to be experienced by bone cement in a clinical implant situation are still real and, in an unconstrained specimen, may be associated with significant deformation.

To summarize, the viscoelastic properties of the polymethylmethacrylate based cements are broadly similar, whether they are assessed by studying creep or stress relaxation, and whether the testing is done in four point bending, tension or compression. They are maximal immediately after polymerization (i.e. at ''set time'') and become less obvious the longer the interval between mixing and testing, due to the ''after cure'' of residual monomer. They are increased with hydrated cement and increasing temperature and by an environment containing fat. The close relationship between the creep curves and the stress relaxation curves, especially with regard to their time course (Figs. 8, 15 and 16), is clearly seen. Since both creep and stress relaxation are different manifestations of the viscoelastic properties of cement, this close association is unremarkable.

As far as the *in vivo* use of cement is concerned, the combined effects of the environmental factors discussed above are difficult and perhaps impossible to assess, but in view of the findings in this study, they certainly cannot be ignored. Adding to these factors the effects of the age of the cement and the complex mechanical effects of *in vivo* vs. *in vitro* polymerization [4] and specimen thickness [5] as well as surgical variability, makes it impossible to predict with accuracy from bench-top or theoretical simulations how any particular specimen of cement will behave mechanically *in vivo*, especially if that specimen is functioning under conditions in which significant stress relaxation may occur [30].

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