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The mechanical properties of recovered PMMA bone cement: A preliminary study

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Abstract Samples of polymethylmethacrylate (PMMA) bone cement, used in the fixation of hip prostheses, have been recovered from 11 patients after in service life spans of between 15 and 24 years. Eighteen samples in total have been recovered from the acetabular and/or femoral cement. Samples were subjected to three point bending tests, their density, porosity and microhardness determined and all specimens were examined using EDX and X-ray techniques. Since the porosity of many of the samples is very high, the continuous matrix properties are inferred from the performance of individual specimens. No evidence has been found to suggest that the PMMA has deteriorated whilst *in-vivo* and the mechanical properties of the cement matrices appear to be comparable to freshly made PMMA.

1 Introduction

PMMA bone cement has been used for the fixation of total hip prostheses for more than 40 years [1, 2]. Since cemented total hip replacement is being used in young patients very frequently, it has become ever more important to determine the properties of the cement over long periods *in-vivo*. Although there are advocates for the use of cementless fixation, particularly in young patients, recent studies indicate that cemented hip stems perform better than non-cemented ones [3, 4]. There are currently more than 20 different PMMA based bone cements commercially available [1].

However, the use of PMMA bone cement is not without potential problems. Some researchers believe that there is scope to improve existing PMMA technology [5]. Others conclude that the presence of fractures, cracks or pores can facilitate the loosening of prostheses [6]. Aseptic loosening of prostheses has been linked to the generation of particles originating from the bone cement as well as from the prosthetic implants themselves [7]. Although PMMA debris generation will be influenced by the design of the prosthesis, it may also depend on the mechanical properties of the bone cement. There have been claims that PMMA, even if initially sound, will have a limited lifespan *in-vivo*, and that the propagation of fatigue cracks within cement mantles is the primary cause of failure in cemented prostheses [8].

In the light of the above, a preliminary study was undertaken of the mechanical properties of PMMA bone cement recovered from patients after significant in-service life spans. In each case the bone cement had been used in the fixation of total hip prostheses. Clinical details of the cases from which the cement samples were retrieved were not sufficient to identify the brand of cement used, however, given the age of the cement and knowing that the range of cement brands commonly available at the time were limited to Palacos®, CMW® and Simplex®, it may be concluded that the coloured samples with opacifier containing zirconium were Palacos® cement and, from the X-ray appearance of unevenly dispersed radiopacifier, that the white samples are CMW® cement. Simplex® cement was not positively identified among the recovered samples.

The samples of PMMA bone cement were collected from 11 patients during hip implant revision surgery. These were presented to the University of Exeter by one of the authors (Mr. Michael Clarke, Orthopaedic Research Unit, Cambridge

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Table 1 Clinical data for recovered PMMA samples

Sample	Age of cement at revision (years)	Age of cement as of 2002 (years)	Prosthesis revised	Notes
1	20	26	Charnley	Femur solid. Acetabulum loose with poly wear
2, 3	21	25	Unknown	Femur and acetabulum loose with acetabular poly wear
4	15	18	Stanmore	Femur and acetabulum loose with acetabular poly wear
5	18	21	Charnley	Femur and acetabulum loose with acetabular poly wear
6, 7	24	27	Charnley	Femur and acetabulum loose with acetabular poly wear
8	22	25	Charnley	Femur solid. Acetabulum loose with poly wear
9, 10	16	19	Stanmore	Femur and acetabulum loose
11, 12	15	18	Charnley	Femur and acetabulum loose
13, 14	18	21	Muller	Acetabular solid but with poly wear. Femur loose
15, 16	20	23	Muller	Femur and acetabulum loose with acetabular poly wear
17, 18	22	25	Unknown	Femur solid. Acetabulum loose with poly wear

University, Cambridge, UK). In most cases the samples included material taken from both the acetabular and femoral regions of patients. The PMMA bone cement functioned *in-vivo* for durations ranging from 15 to 24 years. The in-service life for each sample is shown in Table 1, along with the limited clinical information available. A set of specimens made from 1 year old Simplex® cement, manufactured and stored in the University of Exeter laboratories, were also included in the trials. A single three point bend test was also performed on a sample of CMW® cement that was freshly made in the laboratory using a package of cement that had been stored for approximately 20 years in the laboratory.

The mechanical properties of specimens made from the retrieved samples were examined using a range of tests carried out under several different conditions. The aims of these tests were to establish what relationships, if any, could be found between:

1. the various properties being measured
2. the material properties and the test conditions
3. the specimen properties, the duration *in-vivo* and/or the clinical performance of the hip implants.

The principal aim was to establish whether the measured mechanical properties of the retrieved samples were within the limits expected of freshly made PMMA bone cement. From this an inference could then be made as to the likelihood of the bone cement having deteriorated whilst *in-vivo* to the point of being a contributory factor to the need for revision.

The specimen properties that were measured, known or qualitatively assessed were:

1. modulus of elasticity.
2. microhardness.
3. extent of stress relaxation over 3 seconds.
4. specimen density, matrix density and porosity.
5. age and time *in-vivo*.
6. homogeneity – distribution of pores and fault lines, size distribution of pores.
7. type, level and distribution of any opacifier used.

Specimens were tested wet (after equilibration with distilled water) and dry (after equilibration within a silica gel desiccator). An emphasis was placed upon developing tests that were quick, easy to carry out and appropriate for the specimen size that could be produced. The experimental program was orientated towards developing test procedures that could routinely be applied to other specimens in the future.

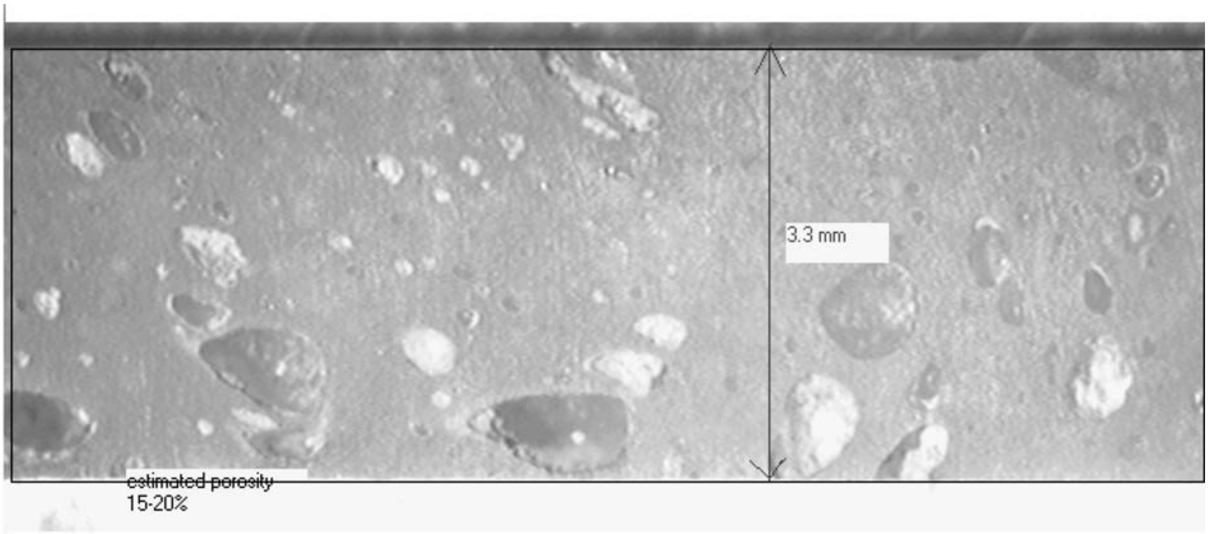
2 Experimental methods

2.1 Measurement of density and porosity

Specimens were weighed following equilibrium with existing laboratory conditions and also following equilibrium within a silica gel desiccator. The nominal specimen density could be calculated by measurement of the specimen dimensions and weight. The matrix density was measured by floatation in solutions of NaCl, $CaCl_2$ and Na_2SO_4. This is in contrast to Martinez-Salazar et al. [10], who used mixtures of cyclohexane and carbon tetrachloride. From the specimen and matrix densities each specimen's porosity could be calculated. The use of floatation to measure matrix density was considered appropriate, given the specimen thickness and the observed range of pore sizes. It is believed that most pores become filled with the surrounding liquid, providing sufficient time for equilibration is allowed. Any shortcomings in this method will lead to an underestimation of matrix density and hence an underestimation of the actual porosity. Magnified images of all specimens were recorded, as these were useful in assessing any lack of homogeneity or the existence of any fault lines within a specimen.

2.2 Three point bend testing

Three-point bend testing was employed to establish the modulus of elasticity and the ability of a specimen to stress relax. Specimens were cut using a slow speed diamond cutting wheel lubricated by a petroleum based oil and were thoroughly rinsed immediately following cutting, then left in distilled water for 24 hours before further shaping. A typical specimen size was 15 × 5 × 1 mm. The specimen thickness was determined by a number of factors. A thickness of more than 1.4 mm would represent too high a thickness to span ratio (affecting the validity of calculation of modulus), could mean that only small deflections could be tested and would limit the number of specimens that could be obtained from each sample. Thicknesses of less than 1 mm were associated with an increased scatter of results, particularly for specimens with large pore sizes (pore sizes could be as large as 0.5 mm) (see Table 2). Figure 1 shows a specimen from sample 1, with a wide range of pore sizes, and a specimen from sample 12 which has very small pores. Because of the limitations in the specimen size that could be produced, it was not feasible to follow ASTM standard test methods. Instead the testing was carried out as was appropriate to the size of specimens that could be produced; an approach that is common for testing miniature specimens [9].



Specimen 1 acetabular

Specimen 8 femur

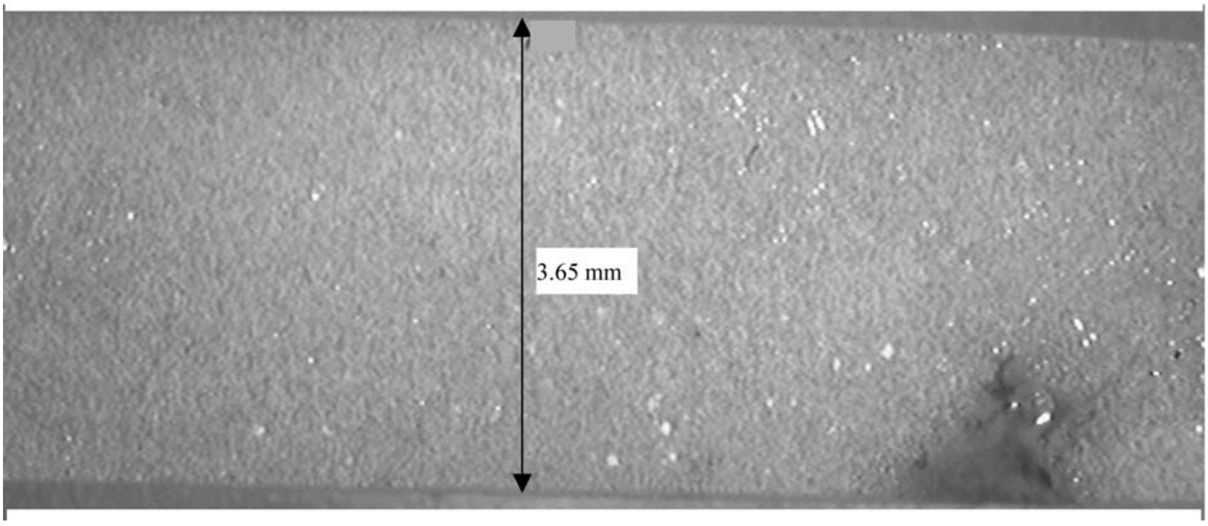


Fig. 1 Photographs of specimens 1 and 12 showing variation in porosity

Table 2 Appearance and density of specimens

Sample	No. of specimens 3-point bend tested	Appearance – (opaque if not stated)	Upper pore diameter (mm)	Most common pore size (mm)	Typical number of pores over 40 μm per 0.8 mm^2	Specimen density range (kg m^{-3})	Matrix density range (kg m^{-3})
1 Acetabulum	4	Milky white	0.8	0.3–0.6	8	920–1020	1103–1151
2 Femur	4	Brown non-homogeneous layers discontinuities and craters present	1.0	0.1–0.15	23	833–900	1085–1133
3 Acetabulum	7	Beige transparent	0.5	0.2	7 –16[a]	888–959	1080–1100
4 Femur	6	Off-white translucent	0.4	0.05 to 0.2	11	962–1056	1100–1135
5 Acetabulum	6	Opaque white[b]	0.4[c]	0.1	14	926- 988	1115–1130
6 Femur	6	Off-white	0.3	0.05–0.15	22	991–1041	1140–1165
7 Acetabulum	6	Off-white	0.3	0.05–0.15	20–40[a]	908–986	1158–1180
8 Acetabulum	5	White homogenous	0.4	0.05–0.2	10	1036–1080	1133–1153
9 Acetabulum	9	White	1.0	0.2–0.5	10	912–1030	1054–1129
10 Femur	6	White	1.5	0.2–0.6	10	975–1101	1129–1150
11Acetabulum	8	White	0.2[c]	0.15	6–16[a]	1021–1151	1156–1188
12 Femur	4	Dark beige	0.3[c]	0.05	16–40[a]	1102–1148	1198–1225
13Acetabulum	9	White	0.5	0.05–0.2	10–30[a]	1017–1111	1097–1133
14 Femur	5	Off-white (dull)	0.3	0.1–0.2	10	1074–1142	1120–1147
15Acetabulum	5	Beige	1.0	0.1–0.2	Over 50	928–1071	1210–1218
16 Femur	5	Beige -	0.4	0.15–0.2	30–50[a]	1039–1171	1185–1223
17Acetabulum	6	Beige, homogenous	0.2	0.05	Over 50	1066–1145	1251–1258
18 Femur	6	Beige, non-homogenous	0.1	0.05	Over 50	1026–1130	1180–1205
Laboratory - Simplex	4	White	0.3	0.2	Less than 5	1229–1251	1240–1251
Lab. CMW	1	White	0.2	0.05	Less than 5	1133	1185

[a] Variable

[b] some dark areas

[c] Elongated pores, smaller dimension given

It was found that there was a significant variation in the mechanical properties of different specimens within a given sample. For this reason a target of at least 5 specimens per sample was set. This minimum number was achieved for all tests except those on sample numbers 1, 2, 12 and the Simplex® and CMW® laboratory made specimens.

Testing was carried out on a micro-tester (Fig. 2) with a fixed crosshead attached horizontally to a load cell. A base slid horizontally towards and away from the crosshead (Fig. 3), with the outer specimen supports attached to the base. The compliance of the unit was checked at regular intervals and was found to be in agreement with the manufacturer's claim. Specimens were held in place by applying a load of around 0.4 N.

Testing took place at a temperature of 22°C ± 2°. It was not deemed necessary to carry out testing at body temperature

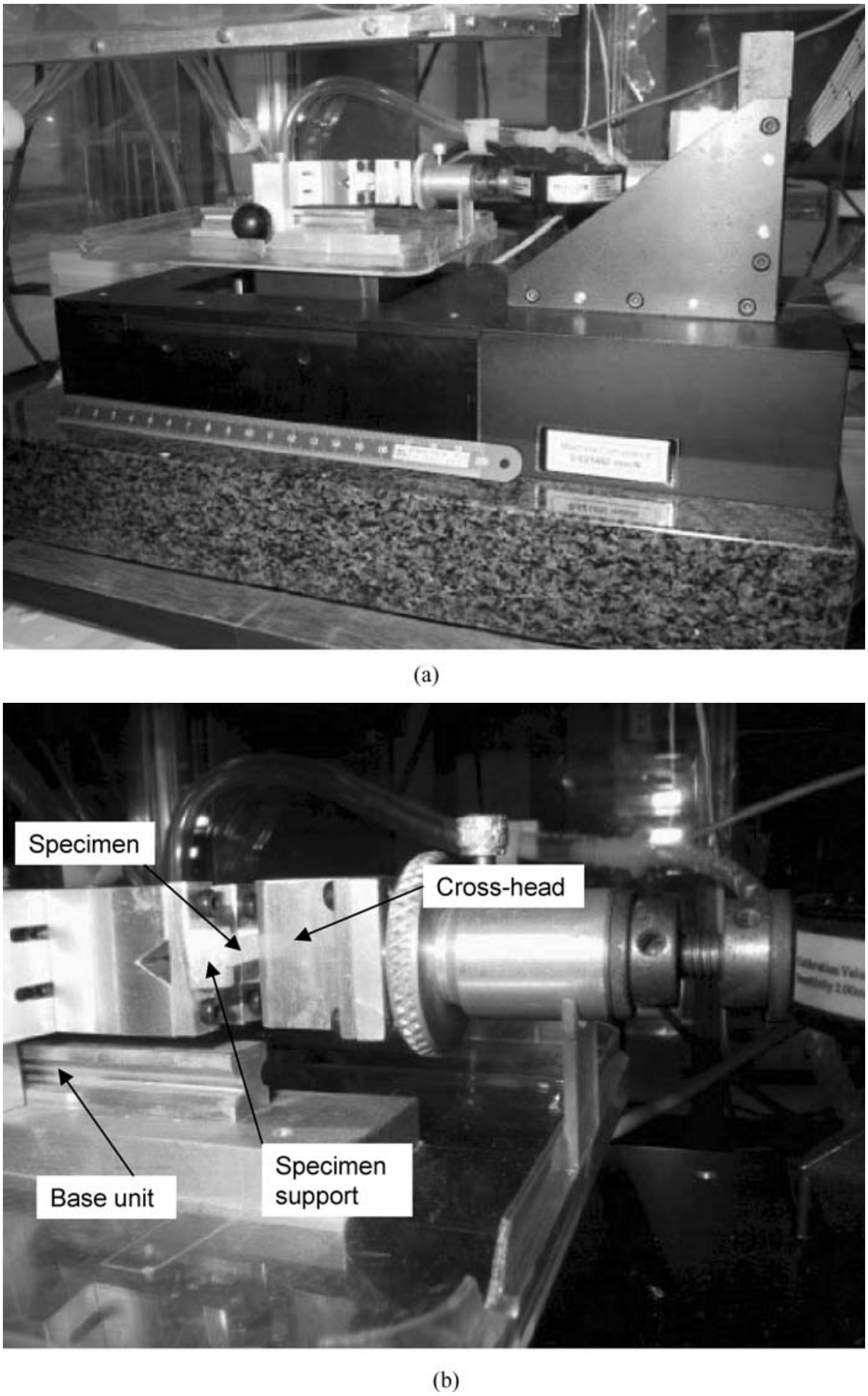
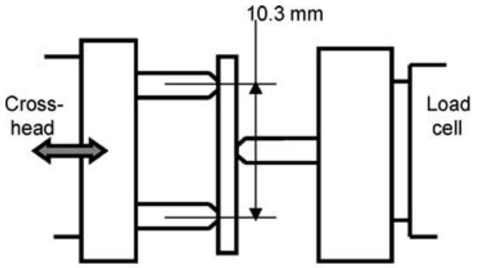
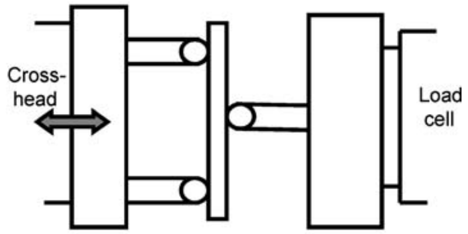


Fig. 2 (a) Microtester for three point bending (b) Specimen in place in microtester



Plan view of three-point bend test arrangement



Alternative specimen supports

Fig. 3 Diagram of three point bend tester showing specimen supports

(37°C) since the aim of the work was to detect any degradation in cement properties over time, rather than absolute values, and there exists a large number of measurements of cement properties at room temperature with which comparisons could be made. When wet testing, specimens were placed immediately into the test rig following removal from water. The testing of each specimen took no more than 5 minutes whereupon the specimen was returned to the water and held for retesting 24 hours later. Investigations were made that included keeping a constant water drip on specimens whilst testing and also testing after the specimen had been placed in the rig, with no water drip, for up to an hour. It was concluded that specimens did not suffer from a rapid change in properties when removed from water and placed in the test rig. For wet testing, the results were accepted if those of the original test and those performed 24 hours later were within 10%.

The three-point bend tester employed flat 1 mm wide specimen supports. The span between inside edges was set at of 10.3 mm for most tests. The deflector head was cut at a 60° angle, with a tip width of 0.18 mm (Fig. 3). Experiments were also carried out using rounded specimen support ends – radius measured at 0.95 mm. The flat and round specimen supports gave similar results, both for load-deflection and for stress relaxation.

The target crosshead-base deflection was set for 1.5 mm, which included approximately 0.6 mm load cell deflection. Loads of up to 4.0 N were permitted. It was established that under these conditions, specimens could be subjected to repeated testing without altering the mechanical performance. Tests were also carried out that indicated that repeated three-point bend testing within these limits did not alter a specimen's microhardness, i.e. microhardness tests performed on specimens that had not been subjected to three point bend testing did not give statistically different results from tests carried out on specimens that had previously been repeatedly subjected to three-point bend testing.

The effects of "relative crosshead to base" speed on calculated elasticity were noted. As the speed was increased from 0.01 mm s^{-1} to 0.03 mm s^{-1}, so the modulus of elasticity increased -i.e. creep was reduced. Increasing the speed to 0.04 mm s^{-1} did not alter calculated values for elasticity. Higher speeds were not explored, since it was considered that there could be a danger of local heating when carrying out repeated tests. A speed of 0.03 mm s^{-1} was adopted as the standard with a 3 second pause between crosshead-base movements. Thus each cycle was as follows:

Specimen loaded over 5 seconds at a crosshead speed of 0.03 mm s^{-1}
Specimen held under constant strain for 3 seconds
Specimen unloaded over 5 seconds at a crosshead speed of 0.03 mm s^{-1}
Specimen held at 0.45 N load for 3 seconds.

This cycle was repeated 5 times for each test. The specimen was then reversed in the testing machine so that the face under tension in the first set of five loading cycles was under compression for a second set of five loading cycles. Prior to the start of any test the specimen was put through 1 preparatory cycle. In order to avoid scatter at low deflections, each cycle was started at 0.45 N load.

Although the "relative crosshead to base" speed used for ISO 5833:2002 [10] tests is 0.083 mm s^{-1}, it should be noted that the distance between points of opposing load is also greater by a factor of approximately 3 for the ISO test. This means that the rate of change of curvature when specimens are bent is approximately the same for ISO tests and for those reported in this paper.

The experimental data show that the load reduces during the 3 seconds strain hold. This was used to calculate specimen stress relaxation. When calculating both the modulus of elasticity and the stress relaxation, the machine characteristics had to be taken into account. The deflection of the load cell under load was significant and also, surprisingly, the equipment (as well as the specimens) appeared to exhibit some tendency to stress relax. The machine characteristics were assessed by performing the standard test, using a metal bar (giving negligible deflection under tests loads) in place of a bone cement specimen. At the test load the metal bar's deflection was negligible so the machine deflection and load relaxation could be directly measured. These could then be deducted from data obtained when using actual specimens.

Three-point bend testing was also carried out on specimens following 7 days equilibration to laboratory conditions and following 15 days in a desiccator. The laboratory-dried specimen test was repeated after 24 hours and further repeats were carried out if the repeat tests were more than 10% different from the first test. Moisture levels within specimens held in the laboratory were typically 0.5–1.5% higher than when desiccated. The modulus of elasticity of laboratory dried and desiccated specimens was within 5% for nearly all cases. The desiccated specimen test was only repeated for 1 set of specimens, for which the initial test results had been unexpectedly low.

The load versus deflection data allowed the modulus of elasticity, in MPa, to be calculated using the standard beam formula:

$$E = \{\mathrm{F.L}^3\}/\{48.\mathrm{I}.\delta\}$$

where E is the Young's modulus of elasticity, F is the force, L is the span, I is the second moment of area of the specimen cross section, δ is the deflection.

Units are N and mm.

2.3 Measurement of microhardness

Initially, microhardness tests were performed on specimens that had not been subjected to three point bend testing; however, it was subsequently shown that three-point bend testing did not alter the microhardness value. Following this observation, microhardness tests were carried out on specimens after three-point bend testing had been completed. Specimens were prepared for microhardness testing by setting in a cold setting resin, soaking for 24 hours in distilled water and polishing using successively finer surfaces. Final polishing was by lapping on a 0.25μ diamond surface using an alcohol-based lubricant. The specimens were then returned to water and left for 24 hours.

Testing used a Knoop indenter with a 1 N load and a 15 second dwell time (dimensions are shown in Fig. 4) and was carried out at 22°C ± 2°C. When testing wet, specimens were removed from water, measurements were made for up to 40 minutes, following which specimens were returned to water for at least 2 hours before further testing. No change in hardness was noted over the 40 minute testing period. Specimens were wet-tested and tested following equilibration in a desiccator. Usually 3 specimens were tested from each sample, with typically 30 indentations per test, made away from any visible pores or cracks.

The Knoop microhardness, in MPa, was calculated from the average indentation length, L, where L is in mm:

$$\text{Hardness H} = 1.423/\mathrm{L}^2$$

2.4 Assessment of radio-opacifier using energy dispersive X-ray analysis (EDX) and X-ray

Specimens were examined using EDX, and the results interpreted using Oxford Instruments' Inca® software. In the first instance an area of 0.03 mm^2 was scanned when searching for evidence of radio-opacifier. If no radio opacifier could be detected at this level, then a higher magnification was employed, focussing on any apparent particulates. The presence of Zr was taken as being indicative of the specimen being formed from Palacos® cement; the presence of Ba and S was taken to indicate CMW® or Simplex® cement. An X-ray appearance of unevenly dispersed radiopacifier indicated that the samples were CMW® cement (at the time the samples were made the radiopacifier was supplied separately with CMW® cement and hand mixed into the polymer powder giving an uneven appearance). Simplex® cement was not positively identified among the recovered samples. As

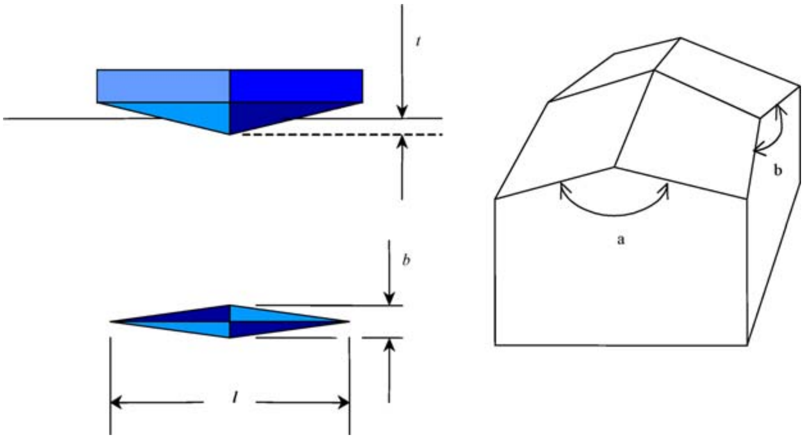


Fig. 4 Profile of Knoop microhardness indenter

noted in Table 2, laboratory made samples of Simplex® and CMW® were also tested.

3 Results

Table 2 summarizes specimen appearance and the range obtained for specimen and matrix densities. The table shows that whilst there is a wide spread in specimen densities - suggesting a random distribution in pores - the matrix densities for specimens from a given sample are usually very similar. This suggests that distribution of the constituents of the continuous matrix has been satisfactory in most cases. Reference to specimens being non-homogenous means that there are apparently boundaries, layers and a variable consistency within the continuous matrix.

Table 3 shows the average Young's modulus and standard deviation for each sample when tested wet and dry. The standard deviation is usually calculated from between 20 and 30 test results.

Figures 5–7 show specimen density (measured dry) versus modulus of elasticity for specimens tested wet and dry, plus the average of wet and dry. The figures show a good correlation between specimen density and modulus of elasticity with R^2 values of 0.7651. 0.8110 and 0.8341.

Table 4 shows microhardness of specimens tested wet and dry. Figures 8–10 show the microhardness values versus modulus of elasticity for specimens tested wet and dry, plus the average of wet and dry. The graphs show a limited

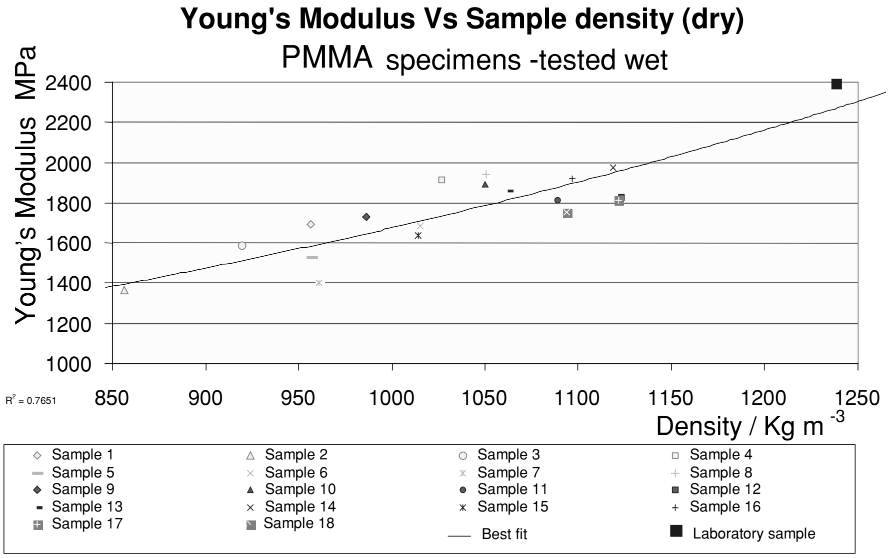


Fig. 5 Modulus of elasticity v sample density, specimens tested wet

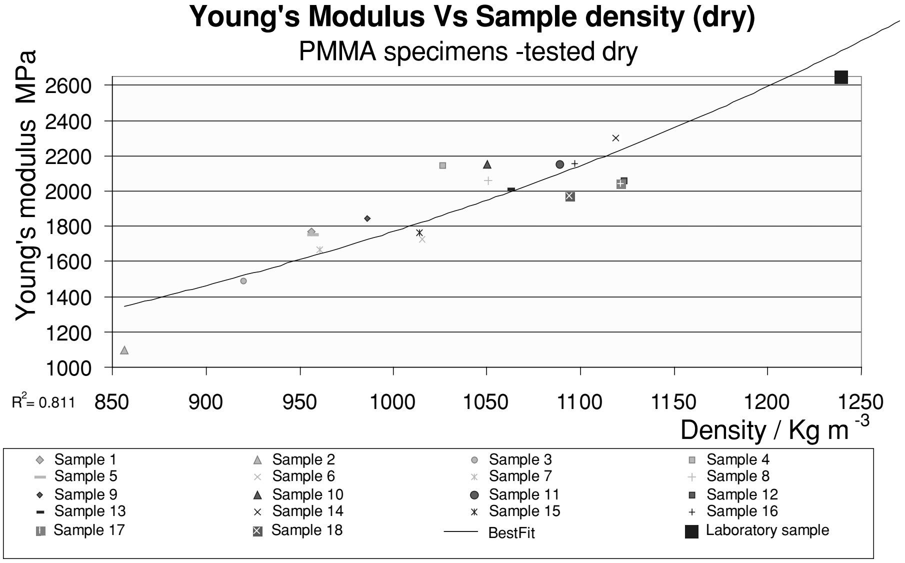


Fig. 6 Modulus of elasticity v sample density, specimens tested dry

Table 3 Average Young's Modulus values and porosity of samples

	Wet samples				Dry samples				
Sample	Young's Modulus (MPa)	Standard deviation (MPa)	Change in sample mean when retested (%)	*P* value*	Young's Modulus (MPa)	Standard deviation (MPa)	Change in sample mean when retested (%)	*P* value*	Sample porosity (%)
1 Acetabulum	1694	319	−3.50	0.602	1770	136	−8.04	0.708	13.6
2 Femur	1363	288	0.63	0.000	1099	49	−2.10	0.000	21.9
3 Acetabulum	1587	418	6.71	0.000	1489	112	−2.34	0.001	16.7
4 Femur	1913	360	– 3.60	0.001	2146	250	−9.07	0.213	6.5
5 Acetabulum	1527	222	0.91	0.007	1752	128	9.60	0.217	14.8
6 Femur	1685	298	– 9.42	0.759	1724	334	9.38	0.009	11.9
7 Acetabulum	1402	195	– 0.12	0.000	1666	199	0.80	0.028	17.7
8 Acetabulum	1944	204	1.21	0.003	2059	196	−4.49	0.175	8
9 Acetabulum	1728	382	– 4.73	0.846	1703	431	−2.13	0.286	13.3
10 Femur	1890	348	– 3.69	0.003	2149	349	−3.07	0.063	7.9
11 Acetabulum	1815	290	– 0.04	0.112	2046	329	1.40	0.020	7
12 Femur	1826	292	– 0.42	0.205	2056	307	−3.67	0.394	7.7
13 Acetabulum	1861	281	– 6.75	0.014	1959	394	−0.10	0.539	4.2
14 Femur	1973	221	0.61	0.001	2301	252	2.25	0.005	1.8
15 Acetabulum	1635	372	−3.30	0.296	1764	406	−7.70	0.112	16.3
16 Femur	1920	153	−0.60	0.008	2155	198	1.40	0.155	9.3
17 Acetabulum	1813	146	0.64	0.169	2044	291	6.70	0.563	10.7
18 Femur	1755	206	– 2.22	0.590	1974	291	−2.22	0.508	8.5
1 year cement - Simplex	2393	145	– 3.61	0.602	2649	177	1.45	0.708	0.4

**P* value indicates the probability that the sample specimens are part of a single population containing the specimens of all samples

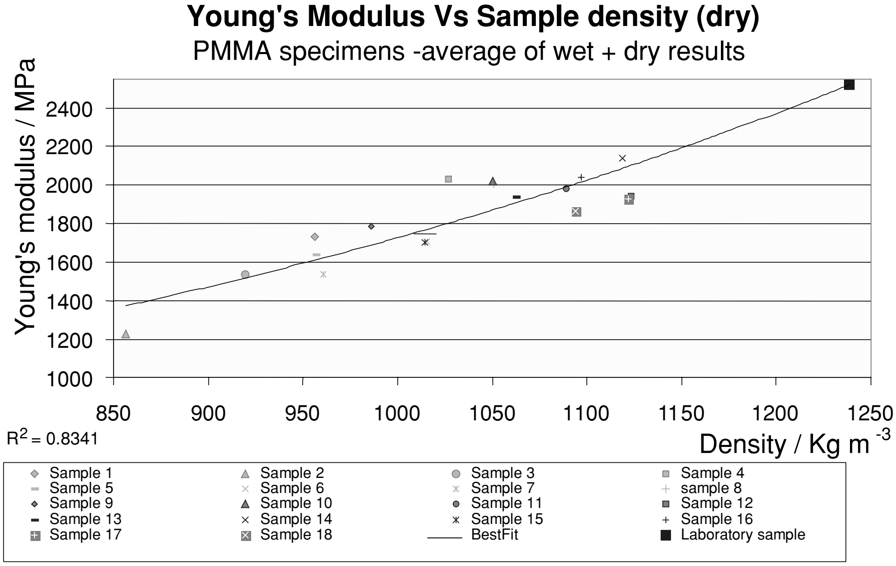


Fig. 7 Modulus of elasticity v sample density, average of wet and dry tests

correlation between microhardness and Young's modulus (R^2 values of 0.3731, 0.6024 and 0.6192), with the average of the wet and dry tests shown in Fig. 10 showing the least scatter.

Table 3 shows the measured values and standard deviation of modulus of elasticity and values of porosity of the samples. Figure 11 shows an excellent correlation between modulus of elasticity and specimen porosity (R^2 values of 0.8367, 0.8120 and 0.8626). A linear response with a low level of scatter has been obtained from tests conducted in both the hydrated and desiccated states. Figure 12 shows experimental results compared to predictions for Young's modulus based on

(i) a volume fraction model for which $E = E_{\text{matrix}}$ {1-porosity}
(ii) an "open cell foam" formula [12], for which

$$\{E_{\text{specimen}}/E_{\text{matrix}}\} = \{\rho_{\text{specimen}}/\rho_{\text{matrix}}\}^2$$

Table 4 Ranges in values for microhardness

	Wet test		Desiccated	
Sample	Mean test result (MPa)	Standard deviation (MPa)	Mean test result (MPa)	Standard deviation (MPa)
1 Acetabulum[a]	15.61	0.585	19.71	1.620
2 Femur[b]	15.13	1.052	18.16	0.353
3 Acetabulum[a]	16.50	0.897	18.49	2.029
4 Femur[a]	16.17	1.070	19.42	1.254
5 Acetabulum	16.39	0.886	19.02	0.616
6 Femur[a]	16.12	0.366	18.70	2.326
7 Acetabulum[a,b]	16.96	0.493	18.99	1.603
8 Acetabulum[a,b]	16.41	1.374	18.94	0.655
9 Acetabulum[b]	17.00	2.020	19.50	0.142
10 Femur[b]	17.02	0.923	19.25	0.197
11 Acetabulum[b]	16.14	1.127	19.23	0.807
12 Femur[a]	16.84	1.038	18.84	0.321
13 Acetabulum	16.56	0.687	19.36	0.921
14 Femur[a]	16.49	0.079	19.41	0.770
15 Acetabulum	15.68	[c]	19.20	[c]
16 Femur	17.33	0.293	20.16	0.122
17 Acetabulum	16.60	0.108	18.99	0.587
18 Femur	16.14	0.143	18.80	0.398
1 year old cement- Simplex	17.80	0.470	20.87	0.416

[a] dry specimens retested with indenter rotated through 90°, average of both sets of results was used

[b] wet specimens retested with indenter rotated through 90°, average of both sets of results was used

[c] insufficient clear area to get meaningful readings on most specimens, only one specimen measured

Fig. 8 Modulus of elasticity v Knoop hardness, specimens tested wet

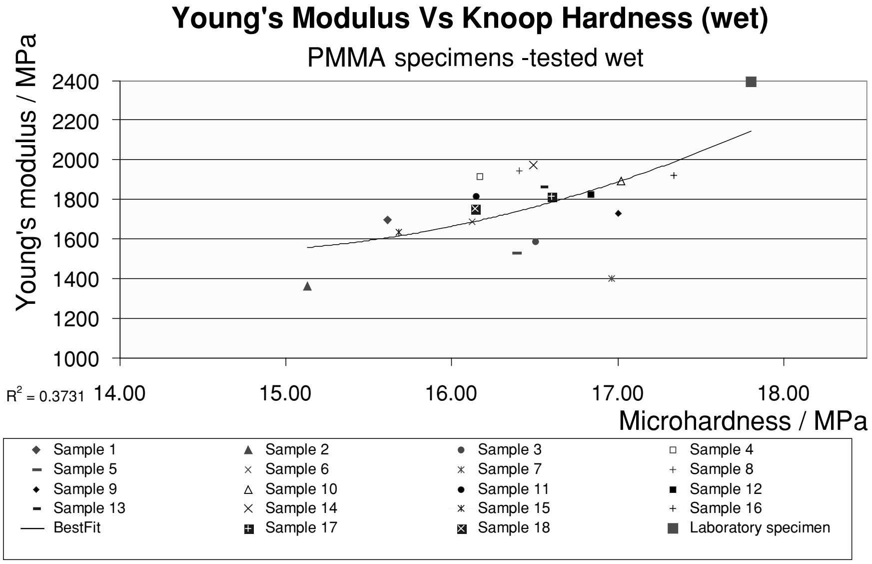
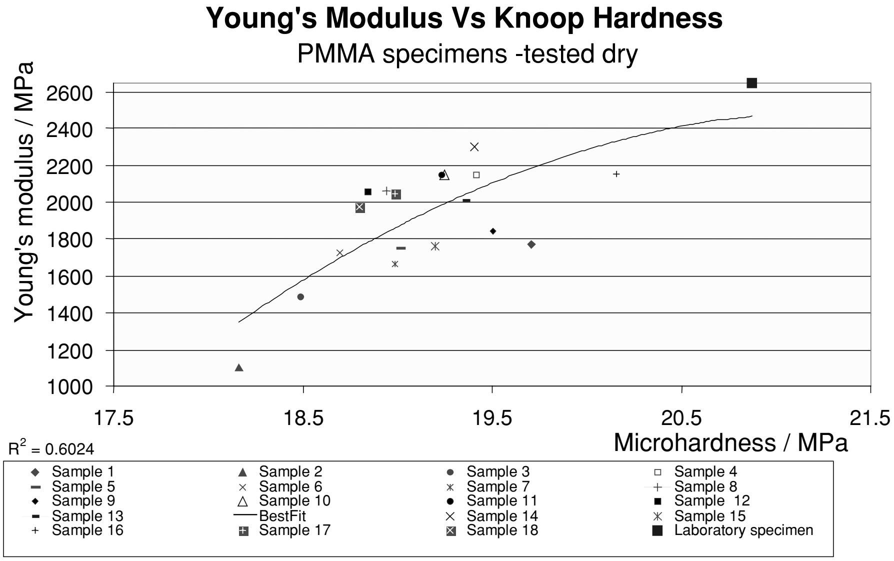


Fig. 9 Modulus of elasticity v Knoop hardness, specimens tested dry



This allows E_{specimen} to be plotted against porosity, given that

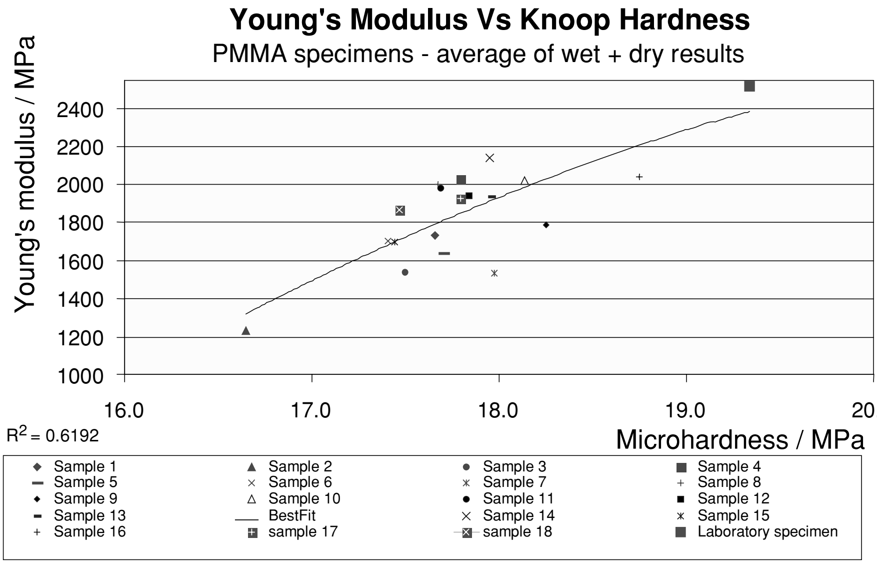
$$\text{Porosity} = 1 - \{\rho_{\text{specimen}}/\rho_{\text{matrix}}\}$$

It can be seen that there is a very close agreement between experimental values of elasticity and those predicted by the open cell foam model.

Table 5 shows the 3-second stress relaxation for each specimen, tested wet, laboratory dried and desiccated. All specimens are shown to exhibit significant stress relaxation, hydrated specimens stress relaxed to a slightly greater degree.

Table 6 indicates the type and distribution of opacifier in specimens, as indicated by EDX and X-ray. The table indicates that specimens that appear beige and have Zr in the radiopacifier are Palacos®. As noted in Section 2.4 above, at the time the cement samples were made in the operating theatre, CMW® cement would have had the opacifier mixed in by hand, giving rise to the discrete particulate distribution noted when using EDX. The laboratory sample of CMW® cement was made using old stock materials, with the opacifier supplied in a separate pouch. The recovered samples appear to match the CMW® laboratory specimen better than the Simplex® laboratory specimen. This is particularly true when considering density as seen on X-ray - the Simplex® cement is much more dense than any of the recovered specimens.

Fig. 10 Modulus of elasticity v Knoop hardness, average of wet and dry tests



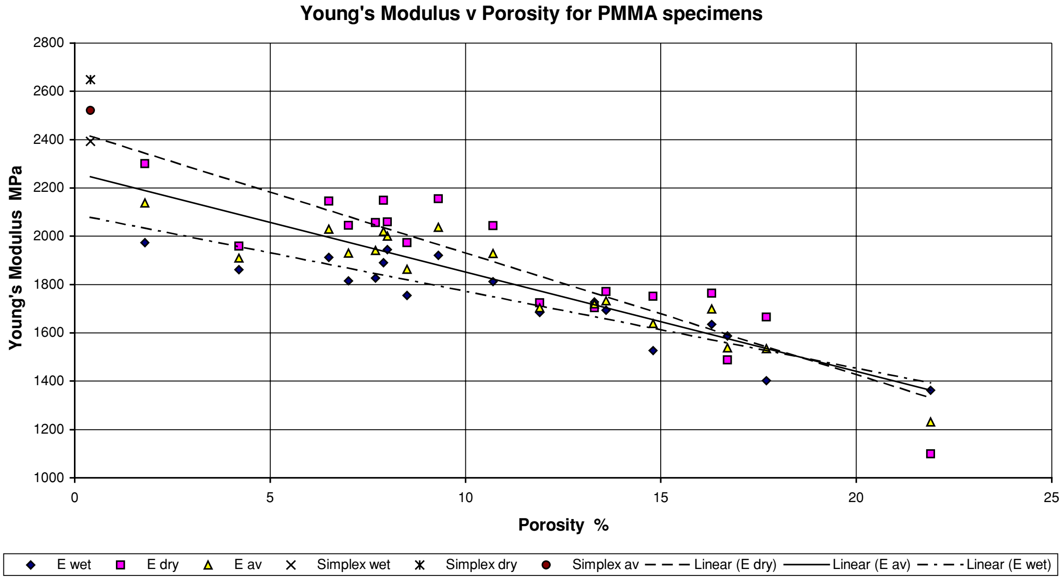


Fig. 11 Modulus of elasticity v porosity, specimens tested wet, dry and averaged

4 Discussion

All the specimens from a given sample would originally have been part of one cement matrix. The variation in properties within each set of specimens indicates that all of the sample cement matrices had large local variations in porosity (when studied using incremental steps across the matrix equivalent to the specimen thickness). This means that the stiffness of each matrix was not a constant but changed from one location to another. It is not clear from this, however, whether these variations were likely to have had a negative effect on the performance of these cement mantles when acting *in-vivo*.

Figures 5–7, showing the relationship between specimen density and Young's modulus, also show that the degree of scatter is slightly less for dry tests compared to wet tests. All five of the samples that showed high density at a given modulus (i.e. were generally below the best fit line) in both wet and dry tests were assessed by EDX as being Palacos® cement. Of the five samples that showed low density in both wet and dry tests, three were white in colour and believed to be CMW® cement, one was white and unidentified and one was off-white and unidentified. This gives a strong indication that the Palacos® cement samples had a higher density to stiffness ratio. The low-density samples are all either CMW® or specimens where the opacifier is at too low a level for

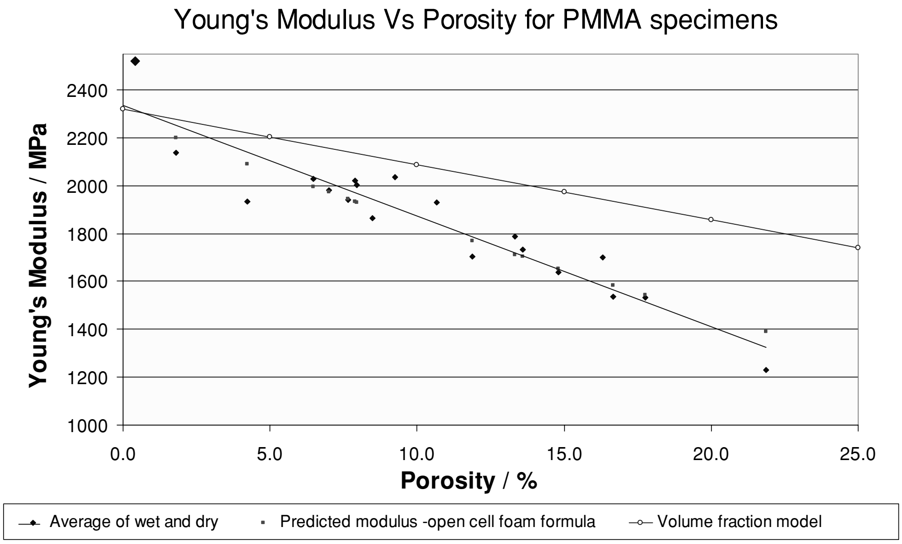


Fig. 12 Modulus of elasticity v porosity, comparison with open cell foam and volume fraction models

positive identification. The result for the laboratory-made Simplex® sample shows a density to Young's modulus ratio that was average for the samples tested.

Microhardness of a sample is primarily related to matrix density. Plotting microhardness against matrix density, porosity and modulus of elasticity shows that, for the specimens tested, the best correlation is between the microhardness and modulus of elasticity (Figs. 8–10) rather than the other fundamental properties. For most samples, fewer specimens were tested for microhardness compared with 3-point bend testing, this is reflected in the higher degree of scatter in results. In most cases 30 indentations per specimen were employed which frequently identified 3 or 4 "soft spots", this suggests that ideally the number of indentations should have been higher.

Since it was not normally possible to orientate the indenter accurately with any known "*in-vivo*" direction, the indenter direction must be considered to be random. The existence or otherwise of anisotropic properties was checked by changing the indenter direction by 90° part way through completing the set of indentations for each specimen. Anisotropic behaviour was not noted for the majority of specimens. The same procedure was followed when performing indentations on dry specimens, with indentations made at 45° to indentations made on the specimens when wet, to ensure that the indentations would not be confused. Table 4 indicates that for

Table 5 Stress relaxation in PMMA samples

	% reduction in load during a 3 -second hold		
Sample	Hydrated	Laboratory dried	Desiccated
1 Acetabulum	2.22	1.35	1.46
2 Femur	1.11	1.09	0.89
3 Acetabulum	2.00	1.35	1.24
4 Femur	1.25	1.21	1.16
5 Acetabulum	1.98	1.26	1.26
6 Femur	1.51	1.15	1.05
7 Acetabulum	1.84	1.01	0.95
8 Acetabulum	1.17	1.12	0.94
9 Acetabulum	1.31	1.16	1.33
10 Femur	1.32	0.88	0.86
11 Acetabulum	1.34	1.08	0.86
12 Femur	1.04	0.80	0.92
13 Acetabulum	1.35	1.20	0.99
14 Femur	2.35	1.78	1.95
15 Acetabulum	2.59	1.78	1.94
16 Femur	2.41	1.85	1.97
17 Acetabulum	1.23	1.15	0.72
18 Femur	1.51	1.03	0.89
1 year old laboratory Simplex	2.36	2.36	1.90

Table 6 Assessment of recovered samples using EDX and X-ray

Sample	Appearance	Opacifier indicated by EDX – low magnification	Opacifier indicated by EDX – high magnification	Opacity under X-ray	Deduced cament brand
1 Acetabulum	White	None	None	Low	Unknown
2 Femur	Brown non-homogenous	None	None	Low	Unknown
3 Acetabulum	Beige	None	None	Low	Unknown
4 Femur	Off-white	None	None	Low	Unknown
5 Acetabulum	White	None	Ba/S	Medium	CMW
6 Femur	Off-white	Zr		High	Palacos
7 Acetabulum	Off-white	Zr		High	Palacos
8 Acetabulum	White	None	Ba/S	Medium	CMW
9 Acetabulum	White	None	Ba/S	Medium	CMW
10 Femur	White	None	Ba/S	Medium	CMW
11 Acetabulum	White	None	Ba/S	Medium	CMW
12 Femur	Dark beige	Zr		High	Palacos
13 Acetabulum	White	Trace Ba	Ba/S	Medium	CMW
14 Femur	Off-white	None	Ba/S	Low	CMW
15 Acetab.	Beige	Zr		Medium	Palacos
16 Femur	Beige	Zr/trace Mg		Medium	Palacos
17 Acetab.	Beige	Zr/Trace Mg		High	Palacos
18 Femur	Beige	Zr		High	Palacos
Laboratory – Simplex	White	Ba/S		High	Simplex
Lab. CMW	White	Ba/S		-	CMW

some specimens, anisotropic behaviour was suggested when specimens were tested wet and in other cases when tested dry. Where this was the case the number of indentations per specimens was increased from 30 to 60. The two cases where the cement sample was sufficiently intact so as to allow orientation of specimens were for sample 5 and sample 6. For sample 5, specimens were cut so that their longest dimension was in a radial direction - these specimens all appeared to be isotropic. For sample 6, two specimens had their longest dimension running in the direction of the stem insertion and four specimens were cut at 90° to this. The first of these two specimens from sample 6 had an average Young's modulus that was 10% higher than the other four specimens. When considering each individual specimen from sample 6, anisotropic behaviour was noted during dry indenting. For this the indenter was turned at 45° to the direction of stem insertion.

Of the three samples with a high microhardness to elasticity ratio, the two with the highest ratio were Palacos®, the third was CMW®. Four samples showed a low microhardness to elasticity ratio - three of these were CMW® and the fourth was Palacos®. This is suggestive, but not conclusive, that recovered Palacos® cement had a higher microhardness to elasticity ratio. The ratio of microhardness to Young's modulus for laboratory-made Simplex® cement was similar to that of recovered specimens.

When considering high porosity cement mantles, the effective modulus of elasticity when *in-vivo* would probably be greater than when measured on specimens. Within a complete mantle, pores filled with fluid would be able to contribute to the overall mantle stiffness (with hydrostatic pressure preventing the collapse of pores during bending). In prepared specimens this will only happen to a more limited extent, although the effect is still measurable. The evidence for this is that the reduction in elasticity with increasing porosity is more gradual for specimens when they were tested wet than when they were tested dry.

The open celled foam formula [12] is intended to describe structures with 70% porosity and above. If pore sizes were smaller and more evenly distributed it might be expected, over the range of porosity being investigated, that the reduction in modulus of elasticity with porosity increase would be much more gradual, e.g. tending towards a volume fraction model. For the recovered specimens, however, the pore size is large relative to specimen depth, suggesting the possibility of excessive deflection at points of "weakness" (caused by adjacent pores) during 3-point bend testing which could explain why specimen elasticity diminishes so markedly with increase in porosity.

Figures 11 and 12 show an extrapolation back to 0% porosity. This is important because it indicates how each of these cement mantles would behave in a non-porous state. These figures can therefore be interpreted as showing that all of the samples tested would give an acceptable modulus of elasticity if tested at low porosity, with the predicted "low porosity performance" being similar to the 1 year old laboratory-made sample. Kühn [1] tested hydrated specimens made from commercially available cements using the ISO 5833 bend test, with results varying from 1750 to 3100 MPa. The lower acceptable limit for hydrated specimens using the ISO 5833 test is 1800 MPa [1, 11]. Extrapolation of best-fit lines indicates that zero porosity specimens made from the retrieved cement samples would have an Young's modulus of around 2150 MPa when hydrated and 2500 MPa when dry.

The Young's modulus obtained for the Simplex® laboratory-made sample is 10% lower than that obtained by Kühn [1]. This implies that if it had been possible to make larger specimens out of the retrieved samples, then a 4-point bend testing in accordance with ISO 5833 would have returned higher values of stiffness than those shown in this report.

When analysing the average of all sample results it was found that hydrated specimen microhardness was 84% of desiccated specimen microhardness. Hydration also reduced stiffness (Young's modulus) to 92% of its dry value, illustrating the plasticizing effects of water. The relatively low change in stiffness between hydrated and desiccated states has also been noted by Kühn [1].

The stress relaxation shown by retrieved samples was significant under all conditions tested and is shown in Table 5. The greatest stress relaxation was noted for hydrated specimens, which is the response that would be expected of freshly prepared PMMA cement and it is comparable to that noted for laboratory-made cement. No relationship was found between extent of stress relaxation and type of cement.

5 Summary and conclusions

This paper presents a preliminary study of the properties of bone cement recovered from patients after functioning in these patients for between 15 and 22 years. As a relatively small number of specimens have been tested, arrangements are in place to obtain more samples following revision or post mortem examination. Results of the extended testing will be published when they are available.

Although the Young's modulus of most specimens tested was somewhat below that which would be expected of freshly made low porosity PMMA cement, the data indicates that this is due to the relatively high porosity of most recovered samples. Results, as shown in particular in Figs. 11 and 12, indicate that the properties of the continuous cement matrix for each sample are within acceptable limits. This conclusion is drawn on the basis that the property of a continuous matrix can be inferred from the property of a specimen in combination with the porosity of that specimen. Each specimen is assumed to act as a composite beam in which the contribution to the modulus of the porous area is negligible.

It appeared that cements mixed in more recent years had the lowest porosity. Given that modern mixing methods produce relatively low cement porosity, it can be predicted that cement used in the fixing of prostheses today will retain an appropriate level of hardness and elasticity for at least 2 or 3 decades whilst *in- vivo*.

The change in properties of the recovered samples following hydration or desiccation was similar to that expected with freshly made cement. Hydration of the cement decreases the microhardness and modulus of elasticity. The extent of reduction of Young's modulus with hydration was the same for the recovered samples as for fresh cement samples [1]. As with freshly made cement, the degree of stress relaxation in the recovered specimens is significant and increases with hydration.

The modulus of elasticity and microhardness of specimens increases with PMMA density, and decreases with increasing porosity. The degree of scatter on results has been acceptable, despite the limited number of specimens tested and their small size. There is also some indication that the scatter in results may be further reduced if cement samples are sub-divided into different brands of cement. These relationships may both be of interest to those studying the fundamental properties of PMMA cement and be of assistance to future studies into the mechanical properties of other recovered cement samples.

No correlation was found between the mechanical properties and clinical performance or *in-vivo* life span of the cement. With the exception of the highest porosity samples, no indication was obtained that there were significant cracks or fault lines within the cement that were reducing its strength.

Overall there is no evidence to indicate that cement mantle properties deteriorate with age or contribute towards the need for revision of implants. In particular, it is thought very unlikely that any changes have occurred within the bulk cement that would allow excessive prostheses movement whilst *in-vivo*. It should be noted, however, that these tests have not been carried out on cement recovered specifically from stem-cement or cement-bone interfacial areas. The methodology developed in this study will be a useful basis for any further studies aimed towards comparing recovered interfacial cement with recovered bulk cement.

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