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Liquid monomer–powder particle interaction in acrylic bone cement

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Abstract

It is known that the method used to mix the liquid monomer and powder of PMMA bone cement influences the quality of the cement that is used in total joint replacements. Mixing theory indicates that the interaction between the liquid monomer and the powder is affected by a number of parameters, such as cement viscosity and degree of agitation, with this knowledge utilized in the design of cement mixing devices. Therefore, the objectives of this study were to: (i) obtain information on the interaction of the liquid monomer and the powder in the case of an PMMA bone cement, (ii) show how this knowledge can be applied to the design of an automated cement mixing device, and (iii) compare the porosity, bending modulus, and bending strength of one commercially-available cement prepared using the automated mixer and prepared using a conventional mixer that is in current clinical use. Experimental data indicated that increasing the velocity and decreasing the viscosity of the systems produced cement that improved mechanical properties, which may contribute to better mechanical integrity and, hence, reduced tendency for aseptic loosening, of cemented hip implants.

Keywords: Acrylic bone cement; PMMA; Reynolds number; Particle–fluid mixing

1. Introduction

In a cemented total joint replacement, the interface between a prosthetic implant and the bone is filled with polymethyl methacrylate (PMMA) bone cement, whose primary function is to provide a stable interface between the prosthetic implant and the surrounding bone by forming a mechanical bond between the two substrates. Ten-year survivorship of cemented total hip joint replacements (CTJRs) in patients > 60 years of age have been reported to be > 90% [1,2]. Given that cemented total hip implants undergo cyclic loads of up to five to eight times body weight [3], the bone cement is susceptible to failure by tensile stresses [4]. Consequently, de-bonding at the implant-cement [5,6] and/or cement-bone interface because of fracture within the cement mantle may contribute to loss of mechanical integrity and aseptic loosening of the cemented total hip implants [4,7]. According to the Swedish National Hip Arthroplasty Registry with respect to revision hip replacement surgery, 76% of revisions are performed because of aseptic loosening [8]. Therefore the long-term survival of a cemented total joint replacement depends, in part, on the integral properties of the PMMA cement [9]. A number of different factors and properties have been shown to affect the mechanical properties of PMMA bone cement. One factor that affects the mechanical properties is porosity [10–12]. Since pores have been identified *in vitro* as stress-risers and crack-initiators [4,13], higher degrees of porosity may contribute to micro-cracking [14–16]. Furthermore, micro-cracking may also lead to PMMA-particle release, which can provoke local inflammation and osteolysis [17,18].

The method used to mix the liquid monomer and the powder plays a significant role in determining the quality of bone cement produced [10]. A high degree of porosity is found to exist in cement that is inadequately mixed. As a consequence, a plethora of studies have been conducted investigating the parameters/variables that affect the quality of bone cement prepared by different designs and types of cement mixing device [19–22]. However, only limited information has been reported on the principles used in the design of these devices [23]. Two important factors are the depth of penetration of the liquid monomer into the powder (l) as they are mixed, a process that is describable using the Washburn equation, and the associated Reynolds number, Re. The objectives of the present study were to: (i) determine the viscosity–time characteristics of a curing cement and to uti-

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lize these results to calculate the depth of penetration, l, and Re; (ii) show how l and Re were used in the design of an automated cement mixing device; (iii) compare variability of the porosity of the cured cement and its bending modulus and bending strength, when mixed with this device compared to the values when the cement was mixed using a commercially-available vacuum cement mixer that is in current clinical use.

2. Liquid monomer–powder particle interaction

It is known that the polymerisation reaction is initiated the instant that the liquid monomer comes into contact with the powder. Therefore, the molecular weight of the liquid monomer starts to increase with a resultant increase in viscosity. Generally, the depth of penetration of a liquid, l, into powder agglomerate is dependent upon viscosity and can be represented by the relationship derived from the Washburn equation (Eq. (1)) [24].

$$l = \sqrt{\frac{Kt\gamma_{L/V}\cos\theta}{2\mu}} \quad (1)$$

where, t is the time (s); $\gamma_{L/V}$ interfacial free energy at the liquid vapour interface (N m^{-1}); θ the angle created between the liquid, vapour and solid interface (°); K size factor which accounts for the complex path formed by the channels between particles (m); μ is the Viscosity of the liquid (Pa s).

The particle Reynolds number for a particle–fluid system can be defined as:

$$Re_P = \frac{d_P v \rho}{\mu} \quad (2)$$

where d_p is particle diameter (m), v relative velocity between particle (m s^{-1}) and fluid, ρ is fluid density (kg m^{-3}) [25].

It is noted that for the Washburn and Reynolds number analyses that: (i) experimental data for the viscosity of the curing cement are needed in order to obtain l and Re; (ii) the Washburn equation is applicable regardless of the order of adding the constituents to the mixer (liquid monomer first followed by powder or vice versa); and (iii) there is a critical Reynolds number at which improvement in the homogeneity of the mixture ceases.

3. Design principles of new automated mixer

The insights obtained from the Washburn and Reynolds number analyses were subsequently used in the design of an automated device for liquid monomer–powder mixing. In the Reynolds number analysis, as particle size and fluid density are essentially constant, in order to initiate the mixing with a modestly high Reynolds number ($Re > 0.2$, limit of Stokes Range which would ensure good mixing), the relative velocity of the particles and fluid would need to be approximately 0.5 ms^{-1}.

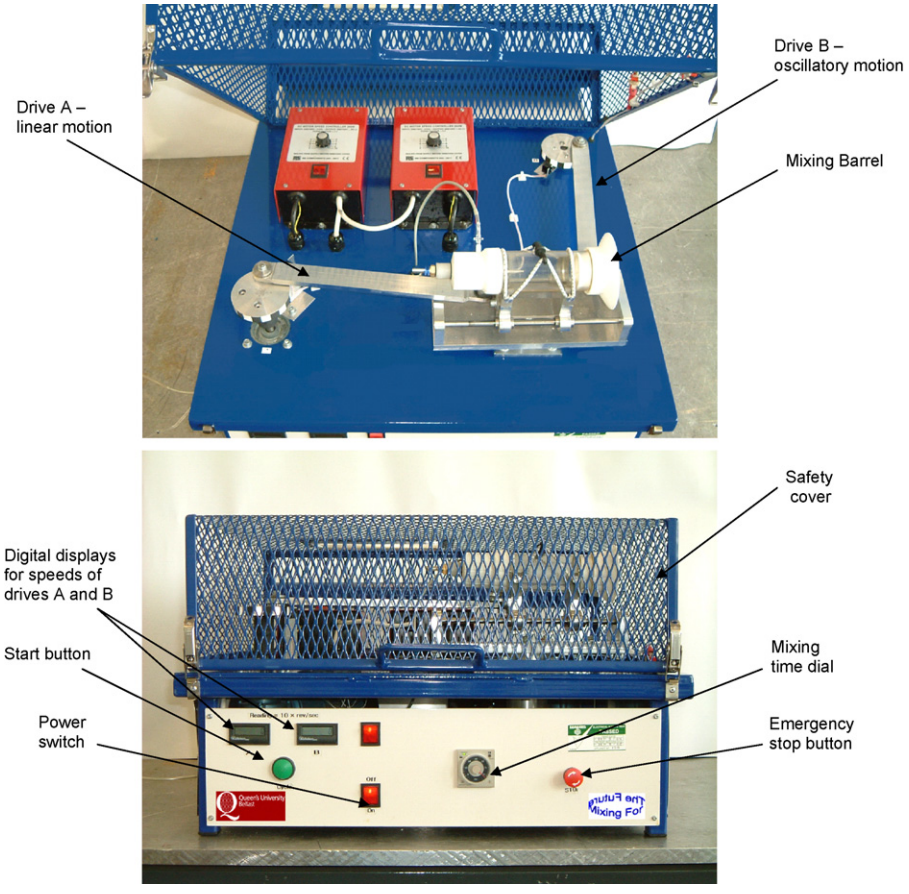

Fig. 1. QUB Automated acrylic bone cement mixing device.

As the viscosity of acrylic bone cement increases quite rapidly with time, the Reynolds number and Washburn analyses indicate, respectively, that non-laminar mixing and significant depth of penetration of liquid monomer within the PMMA powder matrix, can only occur within a relatively short initial time frame. From this analysis a mixing device was designed to increase the relative velocity of the cement components and to impart an increase in mechanical energy to the system over a relatively short time interval.

The device, illustrated in Fig. 1, consists of two cranks which provided linear (drive A) and oscillatory (drive B) motion to a mixing barrel in which the cement components were mixed. A commercial mixing barrel (CMW Laboratories Ltd., Blackpool, UK), with the mixing blades removed was used, and was held in the horizontal position by two barrel holders. The use of a commercial barrel allows the cement to be delivered post-mixing in the conventional manner. A standard vacuum (−86 kPa) was applied during the mixing procedure.

Furthermore, it was envisaged that an automated mixer would ensure that: (i) mixing is performed in a consistent and reproducible manner, and (ii) the inter-user variability in cement quality that has been found in commercially-available third generation vacuum mixing systems [26] would be substantially reduced or possibly eliminated.

4. Materials and methods

4.1. Bone cement

The PMMA bone cement formulation used was the commercially-available CMW® 1 (CMW Laboratories Ltd.).

4.2. Mixing devices

Two mixing devices were used. One was a hand-operated "third generation" commercially-available cement mixing system designed by CMW (CMW Laboratories Ltd.) for use with CMW1® bone cement, which consisted of a cartridge that serves as both mixing and delivery vessels. A vacuum of 86 ± 1 kPa was applied during the mixing stage, and then the mixing paddle was removed and replaced by a nozzle for cement delivery. During the mixing step, the velocity of the blades positioned within the mixing chamber was estimated under normal manual operation (120–150 rpm) to be 0.1 m s^{-1}, producing a maximum shear rate of approximately 1–2 s^{-1}. The mixing time for both devices was 180 s. The other device was the automated mixer (see Section 3).

4.3. Rheology analysis

The complex viscosity [27] of the curing cement was measured using an oscillatory rheometer (Model: TA Instruments 2000), following storage of the cement, for 24 h at 25 and 4 °C. These temperatures were used because cement manufacturers/suppliers recommend that the liquid monomer in some cement brands be stored at room temperature (e.g., Simplex P bone cement, Stryker Howmedica Osteonics, UK) and others refrigerated (e.g., Palacos R bone cement, Heraeus Kulzer, Germany) before it is mixed with the powder for surgery. At each temperature, three shear rates (0.001, 0.01. and 1 s^{-1}) were used. Each rheogram was run in triplicate and the average values are reported.

4.4. Evaluation of cement specimens

4.4.1. Porosity tests

The apparent density of each sample, 75 ± 0.1 mm in length, 10 ± 0.1 mm wide, and 3.3 ± 0.1 mm in depth, was measured using an electronic densimeter. A recent study determined the maximum density using a volume fraction based Eq. (3) [28]. It is noted that the calculated density is obtained assuming 100% conversion or after post-curing of the bone cement. However, in some cases the amount of residual monomer is up to 3–5% (w/w), which may lead to experimental error with this technique. It is also noted that the density measurement for porosity calculated is limited in terms of accuracy. Determination of porosity by micro-computed tomography, although un-available for this study, would allow a higher degree of accuracy.

$$\text{Percentage porosity} = \left(1 - \left(\frac{\text{Apparent density}}{\text{Maximum density}}\right)\right) \times 100 \quad (3)$$

4.4.2. Determination of mechanical properties of polymerised cement

For the determination of the bending modulus and strength, the cement was mixed and rectangular cross-sectioned test specimens (same dimensions as porosity tests) were fabricated, with the properties determined by means of a four-point bend test, following ISO 5833 [29]. For each mixing device, five specimens were tested.

4.4.3. Statistical analysis

All cement evaluation analyses were performed in triplicate batches (of five test samples each). One-way analysis of variance (ANOVA) with a post hoc Fisher's PLSD test was applied to the results for the porosity and mechanical properties, with significance being denoted at $p < 0.05$.

5. Results and discussion

5.1. Viscosity–time characteristics

The increase in complex viscosity over time (Fig. 2) was due to the polymerisation reaction occurring; as the molecular weight of the polymer increased, the viscosity of the liquid monomer increased logarithmically. However, the rate of polymerisation is not constant due to the reduction in the concentration of the monomer (before the gel effect occurs) and the increase in temperature due to heat being absorbed from the surroundings. The variation in the rate of viscosity increase between the initial mixing temperatures is due to the rate of polymerisation decreasing with decrease in initial storage temperature. Therefore, at the lower storage temperature the viscosity increased at a slower rate.

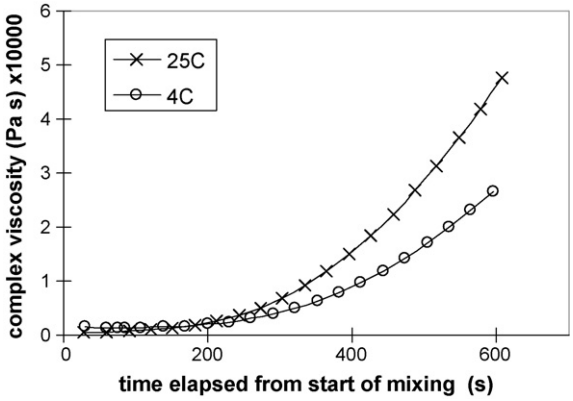

Fig. 2. Effect of initial temperature on viscosity of CMW® 1 acrylic bone cement (Shear rate = 1 s^{-1}). Data obtained using TA Instruments oscillatory rheometer: frequency 5 Hz; platen radius 20 mm; gap 2 mm; lower platen temperature 20 °C.

The results for the effect of shear rate on viscosity (Fig. 3) indicate that the cement shows a degree of pseudoplasticity, in that generally a lower viscosity is experienced with higher shear rates. However, at higher shear rates the pseudoplastic effect decreased, with a slight variation in viscosity found as the shear rate increased from 0.01 to 1.0 s^{-1}. It is also noted that the pseudoplastic nature of the bone cement increased with increase in time and viscosity. It is noted that for $t < 200$ s the viscosity of the cement is virtually Newtonian with only a slight variation in viscosity with shear rate.

5.2. Liquid monomer–powder interaction characteristics

The rheology data illustrated in Figs. 2 and 3, coupled with the powder and liquid characteristics given in Table 1 , were incorporated in the Washburn equation (Eq. (1)) and the expression for the particle Reynolds number (Eq. (2)). These analyses were used to calculate the variation of: depth of penetration, l, and Re with time of mixing.

Fig. 4 illustrates the theoretical rate of liquid monomer–powder penetration versus time using Washburn correlation for CMW 1 acrylic bone cements for storage temperatures of 4 and 25 °C. As the magnitude of the Washburn correlation

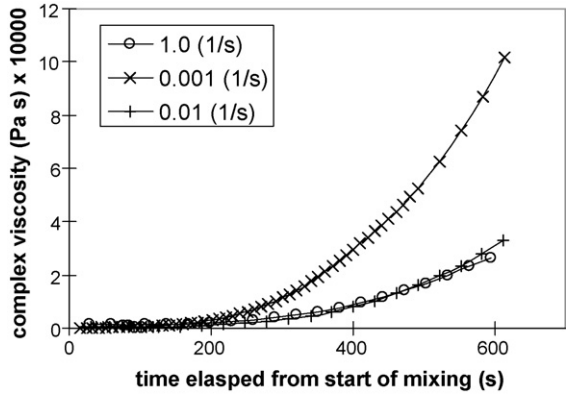

Fig. 3. Effect of shear rate on viscosity of CMW® 1 acrylic bone cement (initial temperature = 4 °C). Data obtained using TA Instruments oscillatory rheometer: frequency 5 Hz; platen radius 20 mm; gap 2 mm; lower platen temperature 20 °C.

Table 1
Characteristics of bone cement mixing system

Surface tension[a]	26.2×10^{-3} N m^{-1}
Contact angle[a]	43° (advancing)
Mean particle size[b]	42×10^{6} m
MMA liquid density[c]	1250 kg m^{-3}
Shear rate (automated)[d]	10 s^{-1}
Shear rate (hand mixer)[e]	2 s^{-1}
Velocity (automated)[d]	0.4 m s^{-1}
Velocity (hand mixer)[e]	0.1 m s^{-1}

[a] Determined using a Camtel Coda 100 surface tension analyzer.
[b] Determined using a Helios laser diffractometer.
[c] Determined by density bottle analysis.
[d] The velocity of the mixing chamber under automated operation was 0.4 m s^{-1}, producing a maximum shear rate of approximately 10 s^{-1}.
[e] The velocity of the blades positioned within the mixing chamber was estimated under normal manual operation (120–150 rpm) to be 0.1 m s^{-1}, producing a maximum shear rate of approximately 1–2 s^{-1}.

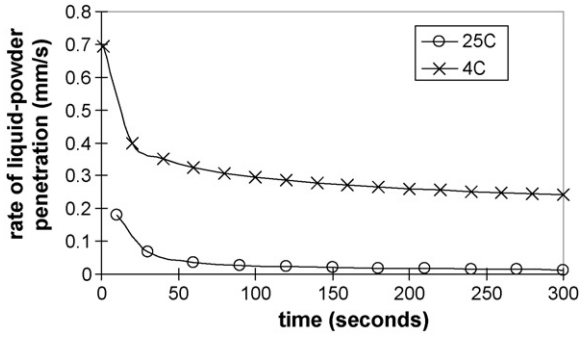

Fig. 4. Theoretical rate of liquid monomer–powder penetration versus time using Washburn correlation for CMW 1 acrylic bone cements.

is dependent on the square root of the cement viscosity, the sharp decrease in the rate of penetration can be attributed to the increase in viscosity during cement curing. The relatively high rate of penetration, found with the cement stored at 4 °C, was due to the polymerisation reaction and dissolution of PMMA beads into the liquid monomer being slower at decreased temperatures.

The data in Fig. 5 indicate that there is an obvious decrease in Reynolds number with increasing time caused by an increase in cement viscosity during the curing process. As with the Washburn analysis, this decrease in Reynolds number is more rapid

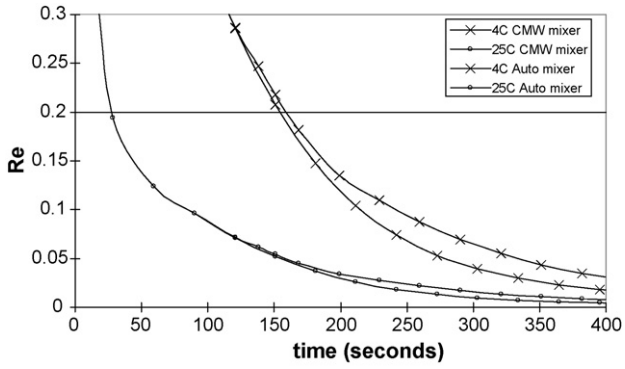

Fig. 5. Particle Reynolds number correlation for CMW® 1 acrylic bone cement under various operating conditions.

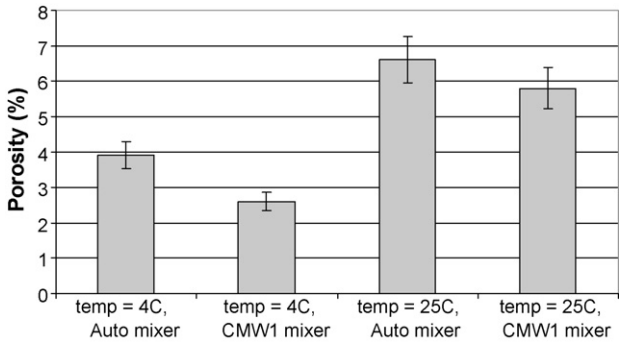

Fig. 6. Effect of mixing conditions on porosity using CMW® 1 acrylic bone cement.

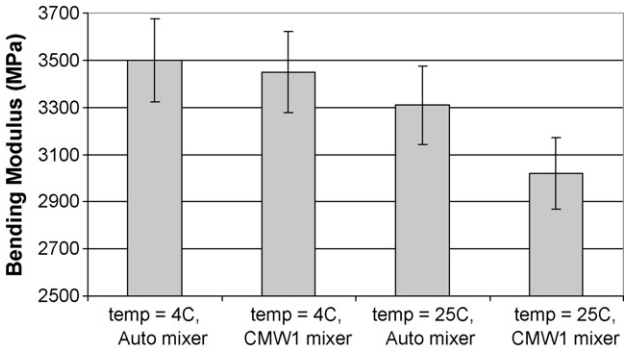

Fig. 7. Effect of mixing conditions on bending modulus of CMW® 1 acrylic bone cement.

with the cement stored at 25 °C compared to the cement stored at 4 °C, due to the factors outlined above. The data in Fig. 5 also illustrate that the rate of mixing of the cement has a smaller influence on Reynolds number, with the higher velocity automated mixing system giving a slightly higher Reynolds number than the CMW system. It is evident from the Reynolds number analysis that the viscous forces predominate within the acrylic bone cement mixing systems. Inertial forces even within the automated mixer are insufficient to maintain Reynolds number above a value of $Re = 0.2$ for more than 150 s. The Reynolds number magnitude of 0.2 was estimated as the limit of the Stokes range at which mixing of discreet PMMA particles was feasible. At lower Reynolds numbers the breakage and transportation of particle agglomerates throughout the cement would still be possible, however the very high viscous forces would prevent individual particle movement.

5.3. Porosity and flexural properties

The porosity data in Fig. 6 indicate that there is a statistical difference between the porosity of the cement mixed at 4 and 25 °C, with the 4 °C cement showing an almost 50% decrease in porosity compared to the 25 °C cement. The decrease in porosity may be attributed to a decrease in air pockets entrained within the cement during mixing. As the sample sets were mixed for the same time period, the material stored at lower temperatures would have a lower viscosity (compared to material stored at room temperature) at the end of the mixing period. This lower viscosity, especially near the end if the mixing period, may have accounted for the decrease in the amount of air entrainment.

The data also indicate a statistical difference between porosity of the cement mixed in the CMW1 mixer and the automated mixer, with the automated mixer giving approximately 20% higher values of porosity. This may be attributed to the higher velocity and to the rolling motion of the cement within the automated mixer causing more air entrainment rather than conventional paddle stirring in the CMW1 mixer.

The bending modulus and bending strength data are given in Figs. 7 and 8 , respectively, these data indicate that there is a statistical difference between the mechanical properties of the cement mixed from different storage temperatures. The 4 °C storage cement shows an approximate 8% increase in bending modulus and a 14% increase in bending strength over the 25 °C storage cement. This may be attributed to a decrease in air pockets of the 4 °C storage cement entrained during mixing, (see porosity data).

The mechanical data also indicate no statistical difference between bending modulus and bending strength of the cement mixed in the CMW1 mixer and the Automated mixer with the 4 °C cement. However, at 25 °C the automated mixer gave approximately 8% higher values of bending modulus and 14% for bending strength.

From these data sets it can be concluded: (i) that lower initial storage temperature results in lower porosity and increased bending strength and bending modulus; (ii) although more air is entrained in the automated mixer (due to the higher velocity), the mechanical properties are at least as good as the CMW1 mixer, probably due to better powder liquid homogeneity.

5.4. Study limitations and clinical relevance

Although the data and analysis presented in this work illustrate the advantage of using an automated mixer that was designed on the principles of liquid monomer–powder interactions, it is noted that *in vitro* properties of the cement may not necessarily be indicative of the properties in a cemented arthroplasty. For example the fact that vacuum mixing is known to decrease *in vitro* porosity of cement, but the clinical results on the beneficial effect of reduced porosity are equivocal [30]. Thus

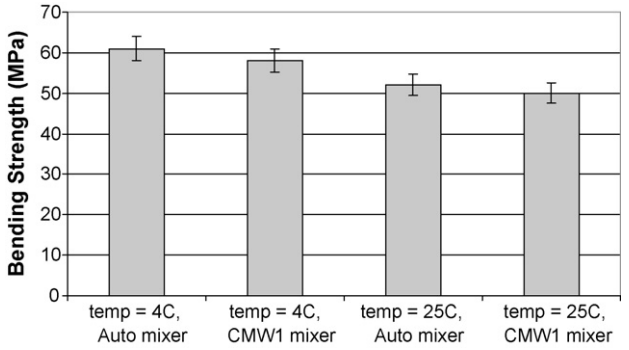

Fig. 8. Effect of mixing conditions on bending strength of CMW® 1 acrylic bone cement.

a more accurate comparison of performance of the automated versus hand operated "third generation" mixers will be in a long-term prospective randomized clinical study of two populations of patients, who received a cemented arthroplasty for which all the parameters (type of implant, design of implant, patient age, surgeon, surgical technique, etc.) are the same, except for the fact that for one population the cement was mixed using the automated mixer and for the other conventional "third generation" mixers. Further work should also focus on the determination of the amount of liquid monomer fumes released into the atmosphere and the cement's fatigue life.

6. Conclusions

(i) The particle Reynolds number analysis indicated that the particle–fluid system was in the turbulent regime less than 100 s (dependent upon mixing system) after which viscous forces dominated due to the rapid increase in cement viscosity caused by MMA polymerisation. It is postulated that within the laminar/viscous regime ($Re < 0.2$, $t > 150$ s, the transfer of mechanical energy imparted from the fluid to the particle would be insufficient to promote effective mixing of the system, and that further mixing ($t > 150$ s) would have minimal effect on improving the homogeneity of the cement.

(ii) An automated mechanical mixing device was designed based on the theoretical analyses, which ensured that mixing is undertaken in a consistent and reproducible manner, so that variables such as mixing time and shear rate could be investigated further.

(iii) Lower initial storage temperature results in lower porosity and increased bending strength and bending modulus. Although more air is entrained in the automated mixer (due to the higher velocity), the mechanical properties of the cement obtained were as good as those obtained when a hand-operated "third generation" mixer was used, probably due to better powder liquid homogeneity within the automated system.

References

[1] E.T.R. James, G.A. Hunter, H.U. Cameron, Total hip revision arthroplasty: does septis influence the results, Clin. Orthop. 170 (1982) 88– 94.
[2] L.D. Topoleski, P. Ducheyne, J.M. Cuckler, A fractographic analysis of in vivo poly (methyl methacrylate) bone cement failure mechanisms, J. Biomed. Mater. Res. 24 (1990) 135–159.
[3] M. Nordin, V.H. Frankel, Basic Biomechanics of the Musculoskeletal System, second ed., Lea and Fibiger, Philadelphia, 1989, p. 22–30.
[4] S.P. James, M. Jasty, J. Davies, H. Piehler, W.H. Harris, A fractographic investigation of PMMA bone cement focusing on the relationship between porosity reduction and increased fatigue life, J. Biomed. Mater. Res. 26 (5) (1992) 651–662.
[5] M. Jasty, W. Jiranek, W. Harris, Acrylic fragmentation in total hip replacements and its biological consequences, Clin. Orthop. 285 (1992) 116–128.
[6] N. Bishop, S. Ferguson, S.J. Tepic, Porosity reduction in bone cement at the cement-stem interface, Bone Joint Surg. (Br.) 78 (1996) 349–356.
[7] M. Jasty, C. Bragdon, W. Jiranek, Etiology of osteolysis around porous-coated cementless total hip arthroplasties, Clin. Orthop. Related Res. (308) (1994) 111–126.
[8] H. Malchau, P. Herberts, T. Eisler, G. Garellick, P.J. Soderman, The Swedish total hip replacement register, Bone Joint Surg. Am. 84-A (Suppl. 2) (2002) 2.
[9] E.L. Masterson, B.A. Masri, C.P. Duncan, Treatment of infection at the site of total hip replacement, J. Bone Joint Surg. Am. 79A (11) (1997) 1740–1749.
[10] L. Vila, Fatigue crack propagation in acrylic bone cements, Adv. Biomater. 10 (1992) 187–192.
[11] N. Dunne, J. Orr, Influence of mixing techniques on the physical properties of acrylic bone cement, Biomaterials 22 (13) (2001) 1819–1826.
[12] G. Lewis, Properties of acrylic bone cement: state of the art review, J. Biomed. Mater. Res. Appl. Biomater. 38 (1997) 155–182.
[13] L.D. Topoleski, P. Ducheyne, J.M. Cuckler, Microstructural pathway of fracture in poly (methyl methacrylate) bone cement, Biomaterials 14 (15) (1993) 1165–1172.
[14] S.K. Bhambri, L.N. Gilbertson, Micromechanisms of fatigue crack initiation and propagation in bone cements, J. Biomed. Mater. Res. 29 (1995) 233–237.
[15] B.A.O. McCormack, P.J. Prendergast, D.J. Gallagher, An experimental study of damage accumulation in cemented hip prostheses, Clin. Biomech. 11 (4) (1996) 214–219.
[16] B.P. Murphy, P.J. Prendergast, The relationship between stress, porosity, and nonlinear damage accumulation in acrylic bone cement, J. Biomed. Mater. Res. 59 (4) (2002) 646–654.
[17] S.M. Horowitz, S.B. Doty, J.M. Lane, A.H. Burstein, Studies of the mechanism by which the mechanical failure of polymethylmethacrylate leads to bone resorption, J. Bone Jt. Surg. 75A (1993) 803–813.
[18] K.F. Hughes, M.D. Ries, L.A. Pruitt, Structural degradation of acrylic bone cements due to in vivo and simulated aging, J. Biomed. Mater. Res. 65A (2) (2003) 126–135.
[19] J.M. Wilkinson, R. Eveleigh, A.J. Hamer, A. Milne, A.W. Miles, I. Stockley, Effect of mixing technique on the properties of acrylic bone-cement: a comparison of syringe and bowl mixing systems, J. Arthroplasty 15 (5 (August)) (2000) 663–667.
[20] H. Mau, K. Schelling, C. Heisel, J.S. Wang, S.J. Breusch, Comparison of various vacuum mixing systems and bone cements as regards reliability, porosity and bending strength, Acta Orthop. Scand. 75 (2 (April)) (2004) 160–172.
[21] U. Linden, Mechanical versus manual mixing of bone cement, Acta Orthop. Scand. 59 (4 (August)) (1988) 400–402.
[22] G. Lewis, J.S. Nyman, H.H. Trieu, Effect of mixing method on selected properties of acrylic bone cement, J. Biomed. Mater. Res. 38 (Fall 3) (1997) 221–228.
[23] N.M. Kurdy, J.P. Hodgkinson, R. Haynes, Acrylic bone-cement. Influence of mixer design and unmixed powder, J. Arthroplasty 11 (7 (October)) (1996) 813–819.
[24] S. McCullough, F.J. Buchanan, J.F. Orr, G.M. Walker, Effect of temperature and mixing conditions on the quality and consistency of PMMA Bone Cement, Plast. Rubber Compos. 29 (7) (2000) 378–384.
[25] R.H. Perry, C.H. Chilton, Chemical Engineers' Handbook, fifth ed., 1973, chapter 5, p. 4.
[26] N. Dunne, C. Daly, Y. Xu, J. Makem, G. Walker, J. Orr, Development of operator independent bone cement vacuum mixing system for joint replacement surgery, Plast. Rubber Compos. 35 (8) (2006) 318–323.
[27] G. Lewis, M. Carroll, Rheological properties of acrylic bone cement during curing and the role of the size of the powder particles, J. Biomed. Mater. Res. (Appl Biomater.) 63 (2002) 191–199.
[28] Brandrup, Immergut "Polymer Handbook", fourth ed., Wiley, 1999, VI/412.
[29] ISO 5833 2002, Implants for surgery–Acrylic resin cements.
[30] D. Janssen, R. Aquarius, J. Stolk, N. Verdonschot, The contradictory effects of pores on fatigue cracking of bone cement, J. Biomed. Mater. Res. Part B: Appl. Biomater. 74B (2005) 747–753.