J Mater Sci: Mater Med (2007) 18:1711–1717
DOI 10.1007/s10856-007-3021-x

Fatigue crack propagation under variable amplitude loading in PMMA and bone cement

S. L. Evans

Received: 13 July 2005 / Accepted: 5 May 2006 / Published online: 5 May 2007

Abstract Fatigue failure of PMMA bone cement is an important factor in the failure of cemented joint replacements. Although these devices experience widely varying loads within the body, there has been little or no study of the effects of variable amplitude loading (VAL) on fatigue damage development.

Fatigue crack propagation tests were undertaken using CT specimens made from pure PMMA and Palacos R bone cement. In PMMA, constant amplitude loading tests were carried out at R- ratios ranging from 0.1 to 0.9, and VAL tests at $R = 0.1$ with 30% overloads every 100 cycles. Palacos R specimens were tested with and without overloads every 100 cycles and with a simplified load spectrum representing daily activities.

The R- ratio had a pronounced effect on crack propagation in PMMA consistent with the effects of slow crack growth under constant load. Single overloads caused pronounced crack retardation, especially at low da/dN. In Palacos R, similar overloads had little effect, whilst individual overloads at low da/dN caused pronounced acceleration and spectrum loading retarded crack growth relative to Paris Law predictions.

These results demonstrate that VAL can have dramatic effects on crack growth, which should be considered when testing bone cements.

Introduction

PMMA bone cements currently provide the most successful method of fixing hip and knee prostheses, and have many other clinical applications. Although cemented fixation, when performed correctly, can give better clinical results than other techniques [1], in the long term failure of the cement is implicated in various ways in the process of aseptic loosening which leads to the clinical failure of the majority of hip and knee replacements. There is evidence that fatigue failure of the cement occurs [2, 3], and this may lead directly to loosening of the prosthesis. In addition, cracking of the cement may allow wear particles or fluid pressure [4] to reach the bone- cement interface, leading to the formation of distal resorbtion cavities which are difficult to reconstruct and may lead to periprosthetic fractures.

There are various possible modes of failure, including longitudinal splitting of the cement mantle, transverse fractures of the cement and failure of the implant- cement or cement- bone interfaces. All of these develop over many years of cyclic loading and so fatigue processes must play an important role. If these various failure modes are to be properly understood and accurately predicted, a better understanding of the development of fatigue damage in the cement is needed. Despite a large volume of published research, the fatigue of bone cements is not well understood and much more research is needed before fatigue failure can be reliably predicted and avoided.

Most of the published studies of cement fatigue [5–11] have used simple S–N tests on unnotched specimens. The presence of stress concentrations that act as sites for crack initiation has a critical effect on the fatigue life and so many of these studies have identified porosity as an important factor [6–8]. However, it is not clear whether porosity is as important in the clinical setting where there are many other stress concentrations and perhaps cracks due to curing shrinkage. Here crack propagation may be more relevant, and in any case a knowledge of crack propagation behaviour is important given that cement

---

S. L. Evans (✉)
School of Engineering, Cardiff University, The Parade, Cardiff
CF24 3AA, UK
e-mail: EvansSL6@cardiff.ac.uk

mantles are known to contain large numbers of fatigue cracks for much of their life [2, 3, 12]. The number of published studies of fatigue crack propagation in bone cement is relatively small [13–18] and there do not appear to be any published studies of the effects of variable amplitude loading (VAL). Indeed, there is very little information available on the effects of VAL on fatigue of PMMA [19] or other polymers, and the effects of VAL are not well understood even in metals [20, 21].

It is obvious that physiological loads on bone cements will vary widely with different activities such as walking, running, stair climbing and sit- to- stand [21, 22]. There will also be considerable variation with time and between patients. As well as variations in the amplitude of loading, the ratio of minimum to maximum load (the *R*- ratio) also varies, and this may be significant in bone cements where slow crack growth is known to occur [23]. Crack growth may occur under high *R*- ratios approaching constant loading, and this may lead to damage development under sustained loading even though the amplitude and number of cycles are small. This is a significant difference from the behaviour of metals, where the amplitude and number of cycles are usually the major influences on crack growth, and conventional approaches to fatigue life prediction may require some modification to take this into account.

Previous studies of fatigue crack growth in pure PMMA have shown important effects of loading history. Pulos [24] carried out very detailed measurements of crack growth under constant amplitude loading (CAL) and found considerable history dependence associated with the development of different fracture paths through the crazes that develop ahead of the crack tip. The craze may fracture at either surface or through the centre, and the crack path depends on the previous loading history. These effects are not well understood but may be important in bone cements as well. Yuen and Taheri [19] studied the effects of overloads on crack propagation in PMMA, and found significant retardation following overloads. The amount of retardation depended on the crack length, which may indicate an interaction with the development of different crack paths described by Pulos. More pronounced retardation occurred as a result of multiple overloads. If these effects occurred in bone cements, there would be profound implications for the development of damage as a result of physiological loading, and for the methods that are used to test bone cements.

The aim of this study was to undertake some preliminary measurements of the effects of VAL on fatigue crack growth in bone cement (Palacos R), including overloads and spectrum loading representing various activities [21]. Tests were also carried out on pure PMMA in order to start to separate the intrinsic behaviour of the polymer from the more complex microstructural effects that may occur in bone cements.

Methods

The cement used in this study was Palacos R (Schering-Plough, Welwyn Garden City, UK), and its composition is shown in Table 1. The cement was hand mixed and cured under pressure in closed polyethylene moulds to produce plates 10 mm thick. Note that although porosity has a critical effect on fatigue life in *S*–*N* tests, it is much less important in crack propagation tests since the crack path is predetermined. The fracture surfaces were inspected visually after failure to make sure that no significant voids were present. The specimens were incubated at 37 °C for approximately 6 weeks and then stored in ambient laboratory air for a further 3 years. After this prolonged curing period the amount of residual monomer should be minimal, and full curing should have occurred, as would be the case after prolonged implantation. Tests were also carried out on pure PMMA (ICI Perspex).

Fatigue crack growth tests were carried out using CT specimens with $W = 20$ mm or 25 mm. All specimens were nominally 10 mm thick; the thickness of the cement specimens was measured along the crack path using a micrometer. The crack length was monitored using Krak–Gages (model A10, Russenburger Prufmaschinen AG, Neuhausen- am- Rheinfall, Switzerland) and a precision constant current supply and amplifier that was designed for the purpose. This device uses a very accurate voltage reference, a precision resistor and an ultra- low offset drift operational amplifier to control the current through the gauge. A precision instrumentation amplifier is used to amplify the voltage drop across the crack, and the whole system is enclosed in the environmental chamber with the specimen to minimise thermal drift. The resulting output voltage was logged every 10s using a Pico Technology ADC16 data logger (Pico Technology Ltd, http://www.picotech.com). The system was calibrated for the particular size of gauges that were used by carrying out a preliminary test in which the crack length was measured at approximately 0.2 mm intervals using a travelling microscope.

Table 1 Composition of Palacos R bone cement

Component	Amount (g)
Powder (40 g)	
Methylmethacrylate- methacrylate copolymer	33.42–33.86
Benzoyl peroxide (hydrous 75%)	0.20–0.64
Zirconium dioxide	5.94
Liquid (20 ml)	
Methylmethacrylate (stabilised with hydroquinone)	18.424
N,*N* dimethyl *p*-toluidine	0.376
Chlorophyll	0.0004

All tests were carried out at 37 ± 0.5 °C in air, and the loading frequency was 10 Hz throughout. Although higher than most physiological loads, this minimises the effects of slow crack growth and also provided consistency with previous data. Published studies of fatigue in PMMA [19] and bone cements [9] have shown little effect of loading frequency. The loading was applied by a Dartec 9500 testing machine, using Dartec Workbench 95 software to apply the VAL.

Initial tests were undertaken using PMMA specimens under CAL at *R*- ratios varying from 0.1 to 0.9. Further PMMA specimens were tested at $R = 0.1$, with 30% overloads applied every 100 cycles. Palacos R samples were tested at $R = 0.1$, with CAL, with 30% overloads every 100 cycles as before and with a simplified loading spectrum previously developed for testing hip replacement constructs [21] as shown in Fig. 1. A series of tests were also carried out in which individual overloads were applied and the subsequent acceleration and/or retardation was measured. This was repeated several times and the crack growth rate was normalised as a fraction of that immediately before the overload was applied.

To obtain the d*a*/d*N* vs. Δ*K* curves, a series of points were identified, typically at 100 μm intervals. Within each interval, the crack growth rate was calculated as a least-squares fit to all the recorded data points, and Δ*K* was calculated from the average of all the data points. Where crack growth was particularly slow the intervals were subdivided to generate more d*a*/d*N* vs. Δ*K* results.

After failure, selected specimens were prepared for scanning electron microscopy by rinsing with methanol and sputtering with gold. They were then examined using a JEOL microscope, with an accelerating voltage of 5 kV.

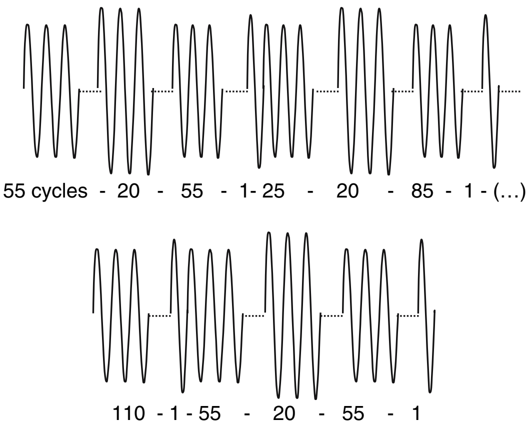

Fig. 1 Simplified loading spectrum developed by Stiles et al. [21]. This is repeated ten times to represent one day of activity. All cycles have an *R*- ratio of 0.1, and Δ*K* is 30% greater for the overloads than for the baseline cycles. Single overloads represent sit- to stand movements and stumbling etc., and block overloads represent running and stair climbing

Results

Figure 2 shows d*a*/d*N* vs. Δ*K* data for pure PMMA at various *R*- ratios. As the *R*- ratio increased, the curves became progressively steeper and moved further to the left, so that the maximum Δ*K* reduced for a given crack growth rate.

Figure 3 shows the effect of applying 30% overloads every 100 cycles on PMMA specimens of two different sizes. There was very pronounced retardation when the overloads were applied, particularly at lower crack growth rates. The crack growth rate was as much as two orders of magnitude lower when overloads were applied, although at higher crack growth rates the effect was reduced. Data from tests on two different sizes of specimen are shown, and the retardation effect was comparable in both although the behaviour of the different size specimens was significantly different. The reasons for this difference are unclear.

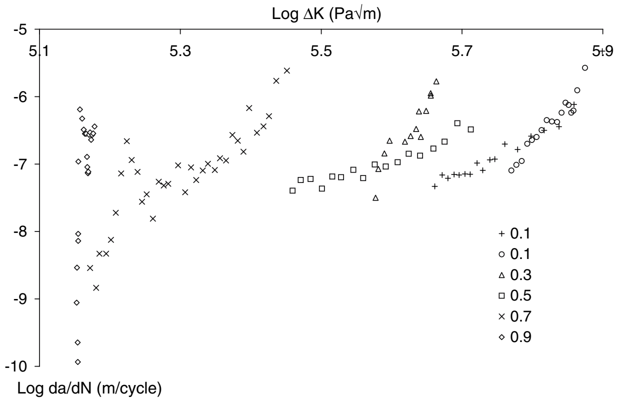

Fig. 2 Fatigue crack propagation in pure PMMA for *R*- ratios varying from 0.1 to 0.9. Data from two different size specimens are included; the reasons for the different behaviour of the different size specimens are unclear

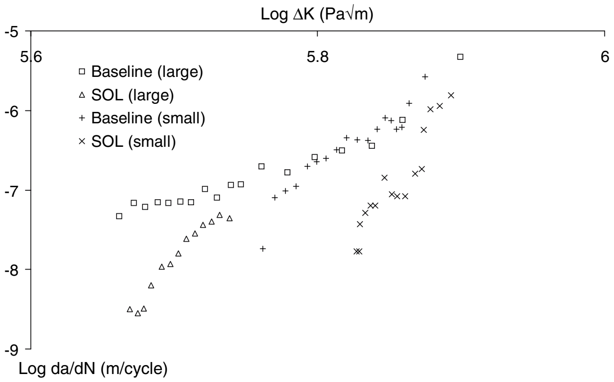

Fig. 3 The effect of 30% overloads applied every 100 cycles on fatigue crack propagation in pure PMMA. At low d*a*/d*N* there is pronounced retardation of crack growth

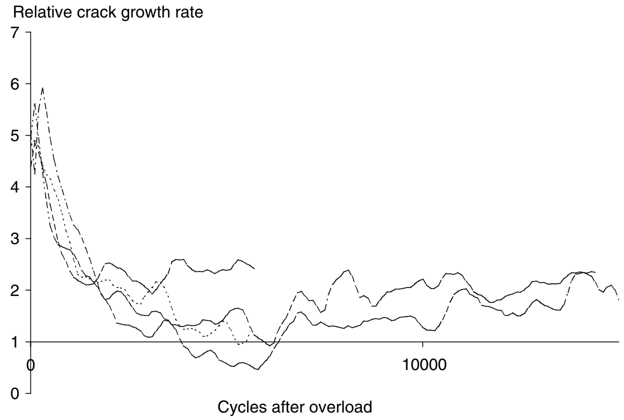

Fig. 4 Crack growth rate after individual overloads in a Palacos R specimen. The graph shows the crack growth rate normalised as a fraction of the crack growth rate before the overload, plotted against the number of cycles applied after the overload. Crack growth after the overloads was accelerated dramatically and there is little evidence of any retardation

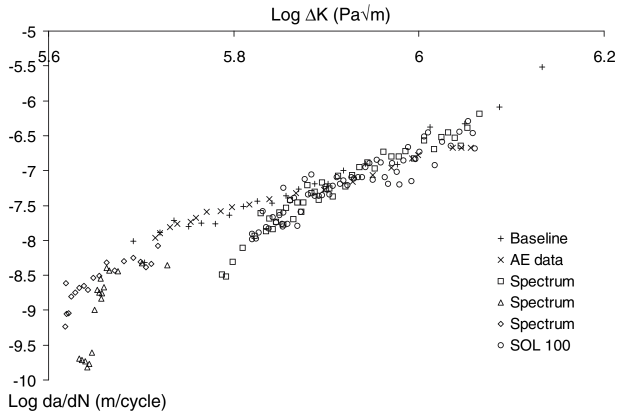

Fig. 6 The effects of overloads every 100 cycles and spectrum loading on Palacos R. The graph shows the same data as Fig. 5, but the crack growth rates have been divided by the expected fractional increase in growth rate due to the overloads, based on the Paris Law. Differences in behaviour are therefore due to anomalous behaviour that deviates from Paris Law predictions

Figure 4 shows the effect of a series of individual overloads applied to a Palacos R specimen. The graph shows the crack growth rate normalised as a fraction of that immediately before the overload was applied (2.97×10^{-9} m/cycle). Almost no retardation occurred, with the crack growth rate accelerating by up to a factor of six after the overload and remaining faster throughout the estimated plastic zone size in almost every case. This is in pronounced contrast to the severe retardation that was observed in PMMA specimens subjected to frequent overloads at low crack growth rates.

Figure 5 shows the effects of single overloads at 100 cycle intervals and spectrum loading on the crack growth rate in Palacos R. In this case, little or no retardation was evident with single overloads, which is very different from the effects that were observed in pure PMMA. Under spectrum loading the crack growth rate was somewhat higher, as would be expected given the large number of higher load cycles.

Figure 6 shows the same data, but with the VAL results normalised using the Paris Law to take into account the effect of the overload cycles. For the single overloads, the Paris Law predicts that the crack growth rate would be 1.044 times greater than for CAL, while for spectrum loading it would be 3.175 times greater. The measured crack growth rates have been divided by these factors to give the equivalent baseline crack growth rate for CAL. With this correction, it is evident that some retardation did occur during spectrum loading, but again this was much less pronounced than in the PMMA specimens.

Figure 7 shows the fracture surface of a PMMA specimen tested under CAL. The fracture surface is initially smooth but longitudinal ridges developed at higher ΔK.

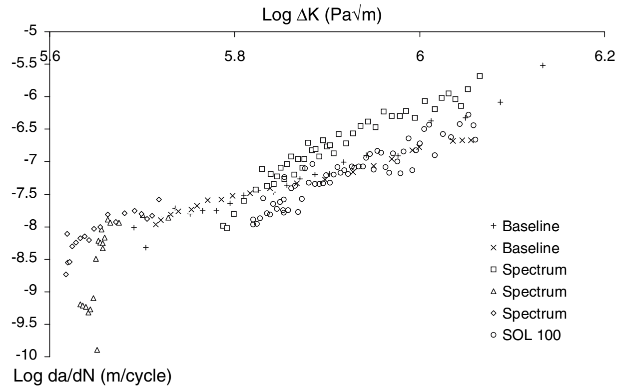

Fig. 5 The effects of 30% overloads applied every 100 cycles and spectrum loading on fatigue crack propagation in Palacos R

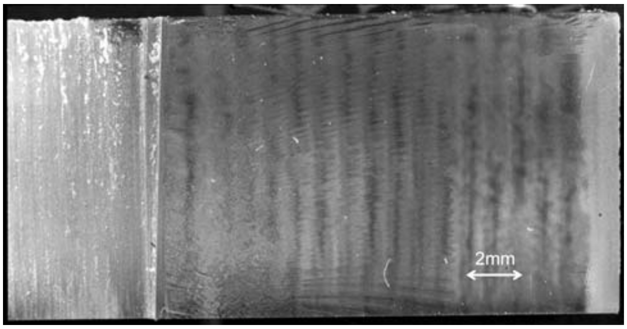

Fig. 7 The fracture surface of a PMMA specimen tested under CAL. The direction of crack growth was from left to right, and the precrack is visible on the left of the picture. The fracture surface is initially smooth, but develops a longitudinal pattern at higher ΔK, and the fast fracture region to the right is very smooth

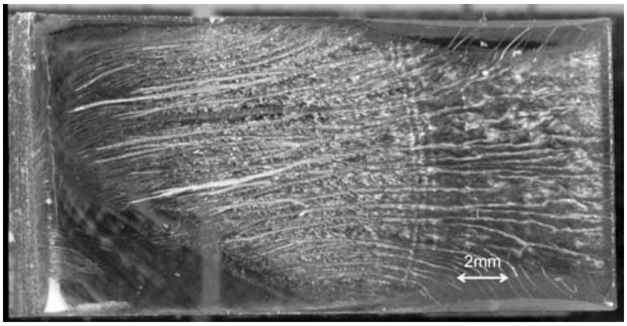

Fig. 8 The fracture surface of a PMMA specimen tested with 30% overloads every 100 cycles. A change in the appearance of the fracture surface from smooth to fibrous is visible, starting in the middle of the specimen- this is the change in crack path described by Pulos. Shear lips are visible indicating pronounced tunnelling of the crack at high ΔK. This did not occur in all specimens

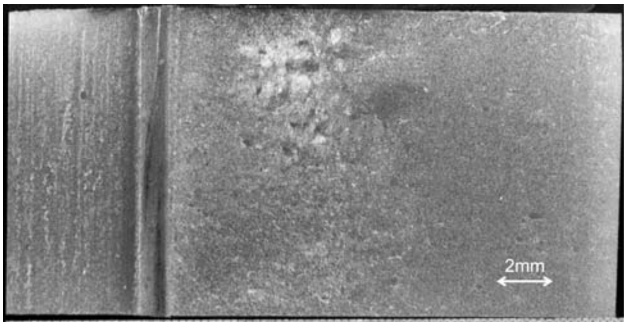

Fig. 10 The fracture surface of a typical Palacos R specimen. The fatigue fracture surface is rough, becoming smooth at the onset of fast fracture. There is no evidence of crack tunnelling or crack path changes, although these might be less clear due to the rough fracture surface

These were seen on many of the specimens irrespective of the type of loading.

Figure 8 shows a similar specimen tested with 30% overloads every 100 cycles. The change in crack path described by Pulos is evident in the fibrous region that spreads from the centre of the specimen. Pronounced crack tunnelling is also evident, as shown by the lips at the edges of the specimen. Both these features occurred in some specimens, irrespective of the type of loading.

Figure 9 shows the fracture surface of a PMMA specimen tested under VAL. Beachmarks corresponding to the overloads are clearly visible, and there is another set of regular longitudinal markings, which are regularly spaced across the crack front. The significance of these markings is unclear.

Figure 10 shows the fracture surface of a typical Palacos R specimen. The surface is macroscopically smooth with no evidence of the crack tunnelling or large-scale crack path changes seen in the PMMA specimens.

Figure 11 shows a scanning electron micrograph of a typical Palacos R specimen. The surface is rough, and the crack has propagated through the pre- polymerized beads with no evidence of the beads pulling out.

Discussion

These preliminary tests showed a variety of interesting effects. At present there is insufficient understanding of the mechanisms of fatigue damage in polymers to explain all of these effects, and the results raise more questions than they answer.

Slow crack growth is known to occur in PMMA and bone cements [23], and the R- ratio is very important for

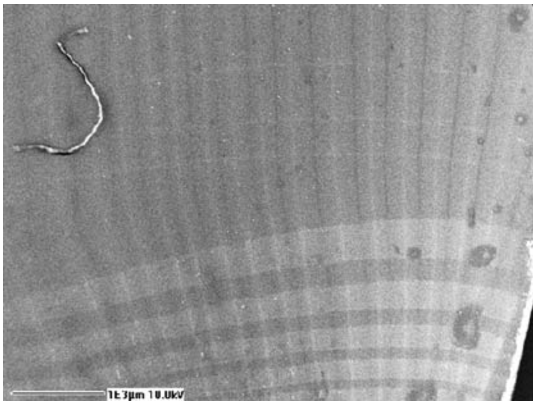

Fig. 9 Scanning electron micrograph showing the fracture surface of a PMMA specimen tested with 30% overloads every 100 cycles. Beachmarks corresponding to the overloads are clearly visible, and there is a second set of longitudinal marks, which are regularly spaced across the crack front. These may represent an alternating crack path through the craze ahead of the crack

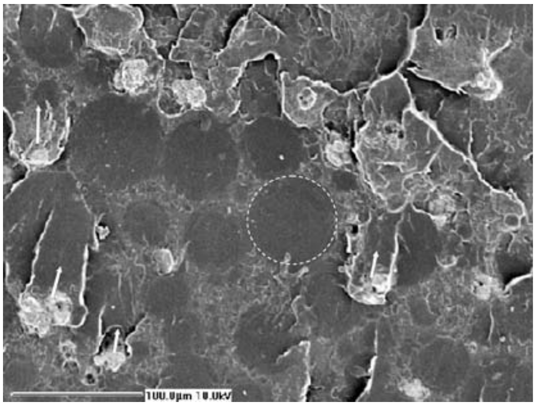

Fig. 11 Scanning electron micrograph showing the fracture surface of a Palacos R specimen. Crack deviation is evident, apparently associated with clusters of radiopacifier particles which may have initiated microcracks ahead of the main crack (arrows show the growth of these cracks). Prepolymerized beads are clearly visible (an example is circled) and there is no evidence of the crack deviating around them

this reason. A high *R*- ratio approaches constant loading and more slow crack growth occurs in this situation. The *R*-ratio had a pronounced effect even at the high loading frequencies employed in this study, and for low loading frequencies or prolonged static loads, this may be much more important. This suggests that prolonged quasi- static loading should be considered in testing as well as the conventional approach based purely on the number of cycles. In the present study, the aim was to isolate fatigue effects from those of slow crack growth where possible, but despite the high loading frequency this was not entirely successful.

Overloads in pure PMMA had a pronounced retarding effect, especially at low ΔK. Paradoxically, occasional overloads made the damage develop more slowly. The reasons for this retardation are not obvious, but presumably the mechanism must involve plastic deformation of the material. In PMMA, this occurs either by crazing or by shear yielding. It can be envisaged that overloads could cause an extension of the craze zone ahead of the crack tip, and that this could have the effect of blunting the crack tip and reducing the crack tip stress intensity, similar to the well-known Dugdale model. On the other hand, very pronounced shear yielding occurs in the plane stress zones, resulting in the pronounced crack tunnelling visible in Fig. 7, and this occurs more at higher ΔK. Overloads could result in more tunnelling of the crack with a subsequent reduction in the effective ΔK due to greater bridging by the shear yielded regions at the edges. It is also possible that crack closure could occur, either by a conventional plasticity- induced crack closure mechanism or perhaps associated with the collapsed craze regions or torn shear-yielded regions. A further mechanism is implied by Pulos's finding of history- dependent changes in the crack path; the development of these changes will probably be influenced by overloads. Further work is needed to identify exactly which combination of these mechanisms is responsible for the observed retardation behaviour.

Several distinctive features were apparent in the fracture surfaces, as shown in Figs. 7–9. The development of a fibrous fracture region, as seen in Fig. 8 and previously described by Pulos, the unusual longitudinal markings visible in Figs. 7, 9, and the pronounced shear lips and crack tunnelling visible in Fig. 8 occurred in various combinations in different specimens, and their occurrence did not appear to be related to the VAL. There was a wide variation in the appearance of the fracture surface even in specimens subjected to apparently identical loading. It appears that the development of these features depends on the specimen size and loading history, but further work is needed to understand the exact nature of this dependence.

In Palacos R, single overloads caused pronounced acceleration of the crack with little or no retardation. Short term acceleration immediately after the overload is common where there is plasticity- induced crack closure [20], but this is usually followed by a more prolonged period of retardation. The cement has a much more complex structure than pure PMMA, including previously polymerised beads and radiopacifier particles, and this results in many microscopic deviations in the crack path, as evidenced by the rough fracture surface (Fig. 11). The frequent small deviations in different directions along the crack front will leave many small ligaments bridging the tip of the crack, and this may account for much of the increased toughness of bone cement relative to pure PMMA. Overloads could enhance this effect, or damage the ligaments and reduce it, which provides a further possible mechanism for overload effects in bone cement. Topoleski [25] suggested that the crack proceeds by microcracking ahead of the main crack tip, which is associated with inhomogeneities in the cement. In this situation, overloads could create a larger zone of microcracking ahead of the crack tip, which could cause more damage ahead of the crack but could also have the effect of blunting the crack or causing more branching, slowing down subsequent crack growth.

Repeated overloads had little effect on the crack growth rate in the cement, although measurements were not carried out at very low crack growth rates and differences might be more apparent there. The large effects seen in the PMMA specimens were not apparent, and it is possible that the microstructure of the cement may prevent the development of crazing and crack path changes over long distances as in pure PMMA. No tunnelling of the crack front or shear-yielded plane stress regions were apparent; possibly shear yielding is inhibited in the cement by the various inclusions. There was no evidence of individual beads pulling out, although this has been widely reported in the literature [6, 25]. One possible explanation could be that the deviation of the crack path around the beads is due to residual shrinkage stresses in the matrix [25] and these stresses may have relaxed in the well- cured and aged specimens in the present study.

The specimens used in these tests were thoroughly cured over several years and would have contained very little residual monomer. This is important since the tests aimed to simulate prolonged fatigue failure over many years *in vivo*, and new specimens that were not fully cured and contained significant levels of residual monomer could behave very differently. Because an electrical resistance technique was used to measure crack growth, it was not possible to test the samples in water. If the specimens had been fully saturated with water before and during testing, some plasticising effect would be expected, which would affect the crack growth rates. Presumably the effects of VAL would also be affected, and since these effects may be associated with plastic deformation around the crack tip, plasticising due to absorbed water might possibly increase the effects of overloads. Further testing is required to investigate this.

Although there was little evidence of retardation when single overloads were applied, there was some retardation under spectrum loading relative to Paris Law predictions. The three different tests on the bone cement specimens thus demonstrated all three possible effects of overloads: acceleration due to individual overloads, no effect from overloads every 100 cycles and retardation under spectrum loading. Clearly the effects of VAL are complex and further work is needed to fully understand the behaviour of the cement.

This study demonstrates that dramatic effects of VAL are possible, and this clearly has implications for the testing and prediction of cements and implant constructs. It is likely that different cements will respond very differently to overloads, depending on their composition and microstructure, and this means that their performance under VAL may be ranked quite differently from that under CAL. Constant amplitude tests could thus be very misleading in comparing the fatigue resistance of different cements. Much more work is needed to understand these effects and to develop better test methods. In the aerospace industry, it is customary to apply loading spectra that represent the varying loads expected in service, and a similar approach should perhaps be applied in biomechanical fatigue testing. However, further work is required to properly understand which loading components and events need to be included and which can be accelerated or omitted.

Conclusions

This preliminary study showed a variety of different effects due to VAL, ranging from retardation of the crack growth rate by up to two orders of magnitude to acceleration by up to a factor of six. A variety of contradictory results occurred and clearly more research is needed to fully understand the effects of VAL.

Current test methods and life prediction models do not take these effects into account, with tests invariably carried out under CAL and models of life prediction assuming linear accumulation of damage. However, these results demonstrate that greater or lesser sensitivity to overloads could completely change the behaviour of cements and constant amplitude tests might be very misleading.

More research is needed to understand these effects and take them into account in developing future test methods. In the future, it may be possible to develop robust spectrum loading tests that incorporate all relevant loading events and accelerate them where appropriate, as has been done for metals in the aerospace industry. This study demonstrates that such an approach may be necessary for testing orthopaedic implants and materials, if truly meaningful results are to be obtained.

References

1. A. FAULKNER, L. G. KENNEDY, K. BAXTER, J. DONOVAN, M. WILKINSON and G. BEVAN, *Health Technol. Assess.* **2(6)** (1998) 1
2. M. JASTY, W. J. MALONEY, C. R. BRAGDON, D. O. O'CONNOR, T. HAIRE and W. H. HARRIS, *J. Bone Joint Surg.* **73B(4)** (1991) 551
3. P. Erani, P. Savigni, L. Cristofolini and M. Viceconti, In Proc. of the European Society of Biomechanics, 's-Hertogenbosch, Holland, July 2004
4. P. ASPENBERG and H. VANDERVIS, *Acta Orthop. Scand.* **69(1)** (1998) 1
5. S. K. BHAMBRI and L. N. GILBERTSON, *J. Biomed. Mat. Res.* **29** (1995) 233
6. S. P. JAMES, M. JASTY, J. DAVIES, H. PIEHLER and W. H. HARRIS, *J. Biomed. Mat. Res.* **26** (1992) 651
7. N. DUNNE, J. F. ORR, M. T. MUSHIPE and R. J. EVELEIGH, *Biomaterials* **24** (2003) 239
8. J. P. DAVIES and W. H. HARRIS, *Clin. Orthop. Rel. Res.* **254** (1990) 261
9. G. LEWIS, S. JANNA and M. CARROLL, *Biomaterials* **24** (2003) 1111
10. M. BALEANI, L. CRISTOFOLINI, C. MINARI and A. TONI, *Proc. Instn. Mech. Engrs., Part H, J. Eng. Med.* **217(1)** (2003) 9
11. G. LEWIS, *J. Biomed. Mat. Res.* **66B(1)** (2003) 457
12. L. CRISTOFOLINI, A. S. TEUTONICO, L. MONTI, A. CAPPELLO and A. TONI, *J. Biomech.* **36(11)** (2003) 1603
13. C. M. RIMNAC, T. M. WRIGHT and D. L. MCGILL, *J. Bone Joint Surg.* **68A** (1986) 281
14. N. C. NGUYEN, W. J. MALONEY and R. H. DAUSKARDT, *J. Mat. Sci.: Mater. Med.* **8(8)** (1997) 473
15. S. ISHIHARA, A. J. MCEVILY, T. GOSHIMA, K. KANEKASU and T. NARA, *J. Mat. Sci.: Mater. Med.* **11(10)** (2000) 661
16. J. M. MANERO, M. P. GINEBRA, F. J. GIL, J. A. PLANELL, J. A. DELGADO, L. MOREJON, A. ARTOLA, M. GURRUCHAGE and I. GONI, *Proc. Instn. Mech. Engrs., Part H, J. Eng. Med.* **218** (2004) 167
17. S. SCHMITT, D. J. KRZYPOW and C. M. RIMNAC, *Biomed. Tech. (Berl.)* **49(3)** (2004) 61
18. E. Piazza, M. Baleani, L. Cristofolini and A. Toni, In Proc. 12th Conference of the European Society of Biomechanics, Dublin, 2000
19. B. K. C. YUEN and F. TAHERI, *Polymer Testing* **23(5)** (2004) 491
20. M. SKORUPA, *Fatigue Fract. Engng. Mater. Struct.* **22(10)** (1999) 905
21. C. M. STYLES, S. L. EVANS and P. J. GREGSON, *Biomaterials* **19** (1998) 1057
22. G. BERGMANN, G. DEURETZBACHER, M. HELLER, F. GRAICHEN, A. ROHLMANN, J. STRAUSS and G. N. DUDA, *J. Biomech.* **34(7)** (2001) 859
23. P. W. BEAUMONT and R. J. YOUNG, *J. Biomed. Mat. Res.* **9** (1975) 423
24. G. C. PULOS and W. G. KNAUSS, *Int. J. Fract.* **93(1–4)** (1998) 161
25. L. D. T. TOPOLESKI, P. DUCHEYNE and J. M. CUCKLER, *Biomaterials* **14(15)** (1993) 1165