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Prediction of the long-term creep behaviour of hydroxyapatite-filled polyethylmethacrylate bone cements

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Abstract The creep behaviour of bone cements based on polyethylmethacrylate, with and without addition of hydroxyapatite filler has been investigated, in order to determine the effect of hydroxyapatite filling and to investigate methods of predicting the long-term creep behaviour from short-term tests. The materials were produced under laboratory conditions and tested in tension in Ringer's solution, as the study was intended to investigate the inherent materials behaviour rather than to simulate realistic conditions. The effects of adding hydroxyapatite were to increase the short-term stiffness and more significantly to decrease the creep rate. Short-term creep tests of up to 10^6 s were conducted at various temperatures, stresses and ageing states. These were then used to investigate various methods of extrapolation to long-term behaviour. The use of time-temperature superposition was found to be useful, though it takes no account of ongoing physical ageing and so gives a significant overestimate of long-term creep strains. Stress-time superposition was less useful and also excludes ageing effects. The use of 'effective time' theory was more successful, but requires a large number of short-term tests. The most effective method was that of the 'integrated time' approach, which required fewer tests yet still gave good correlations with longer-term data.

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Introduction

Polymer-based bone cements have been used extensively in recent decades as fixation media for prosthetic replacements, and the most widely used are based on polymethylmethacrylate (PMMA). Despite widespread use, there are still some problems with this, and although improvements have been made, implant failure rates are still approximately 5% within 10 years. A recent and extensive survey from Sweden [1] shows that implant loosening is the most significant cause of failure, accounting for at least 60% of cases. Over 80% of these implants were cemented, with PMMA-based materials used in all cases. Such implant loosening is often attributed to failure of the bone cement [2–4], either by debonding from the interface, debonding from any filler particles or crack formation due to creep and fatigue. Some other issues associated with the use of PMMA based cements include chemical necrosis due to leaching of unreacted monomer from the cement, thermal necrosis due to the relatively high curing exotherm of PMMA cements and shrinkage on curing causing implant loosening. In addition, the mechanical properties of the PMMA cements pose some concerns, with their low toughness potentially leading to crack formation under long-term creep and fatigue loadings [5].

Although cementless arthroplasties have been developed to obviate these problems, they are not without their own drawbacks and still account for less than 20% of replacements [1]. Another possible solution would be to use a more flexible and tougher bone cement, and investigations into polyethylmethacrylate (PEMA) and polybutylmethacrylate (PBMA) have been undertaken. These materials do have some attractive benefits, including lower modulus and higher toughness, which will help to reduce crack development. For instance, the modulus and strain to failure for

PEMA cements are typically 700 MPa and 50% respectively, compared with about 2,500 MPa and 10% for PMMA based cements. Greater localised yielding with these materials will also lead to favourable stress redistribution, which will reduce local stresses [6]. They also tend to have lower rates of monomer leaching [7], and as the EMA and BMA monomers are less toxic than the MMA monomer [5], this would reduce the potential for chemical necrosis. The curing exotherm is also smaller [8, 9], reducing the tendency for thermal necrosis. The major drawback with these polymers, however, is the higher creep rate than seen with PMMA cements, and so there is significant potential for subsidence of the implant, due to excessive creep deformation in the cement rather than any fracture. This poor creep resistance has so far prevented the commercial development of PEMA based cements.

Various studies into the creep behaviour of bone cements have been undertaken [10–14] which have allowed some limited finite-element modelling of long-term behaviour to be undertaken [15]. Where studies have compared PMMA cements with those based on PEMA or PBMA [11, 12], it has been found that the creep rates and stress relaxation rates are significantly higher with the PEMA and PBMA. It should be noted that there is a danger of over-exaggerating the effects of creep, as the significant constraints present in service have been shown to reduce creep rates [16].

In order to appreciate the effects of creep, it is important to establish the stress levels within the bone cement, and various studies have used element-based modelling techniques to establish the stress distributions. As the bone cement is a viscoleastic/viscoplastic material, it is important to attempt to model the time-dependent and yielding behaviour. Any attempts using purely elastic properties will lead to over-estimates of the stresses. Crowninshield et al. [17] used a finite element model that included localised yielding of the bone cement. They concluded that the maximum stress predicted with a PMMA cement was about 2.8 MPa. They stated that as this study did not include any time-dependent effects, creep and stress relaxation would lead to the stress values decreasing with time. The effect of cement modulus was seen as important in this case. Although they found that a lower cement modulus caused an increased stress in the stem, the stress in the cement decreased, and as cement failure or deformation is the major problem, it was seen as beneficial to have a lower cement modulus. Wheeler et al. [15] included a creep component to finite element modelling of PMMA cements and showed that the peak tensile stress in the cement rapidly dropped to below 2 MPa, with shear stresses between 2 and 3 MPa. Both would decrease with time, and with a softer bone cement. Based on these studies, a standard long-term tensile stress of 1 MPa was used for this study on the softer PEMA cement, although some tests were conducted at stresses up to 8 MPa.

The effect of test environment is of obvious importance as the in-vivo environment is likely to affect creep due to plasticisation and some studies of this have been reported in the literature. It has been found that water and physiological salt solutions have a significant plasticising effect on PMMA based cements, giving higher creep and stress relaxation rates [18, 19], with creep rates some 2–3 times greater in water. The effects of fat-containing environments were even greater, with creep rates more than 4 times higher than in air. Similar studies on a PEMA cement showed a significant effect of water, increasing creep rates by some 3–4 times, with no additional effects of physiological salts [20]. Interestingly, the effect of the fat-based environment Intralipid on the creep rate was less than that of water, which is the opposite behaviour to that seen with PMMA [19].

The purpose of this present study is two-fold; first to assess the effects of hydroxyapatite (HA) reinforcement on the creep behaviour of a PEMA based bone cement and second to explore extrapolative prediction methods. The incorporation of hydroxyapatite has several potential advantages. It is likely to reduce the creep rate [21], increase bio-compatibility and reduce shrinkage. It has also been shown to increase fatigue resistance [22]. The drawbacks will be an increase in stiffness and some loss of ductility. There will probably be an optimum level of reinforcement where these factors are balanced. The effects of hydroxyapatite reinforcement on creep have been most extensively studied for polyethylene. Suwanprateeb et al. [23] found that reinforcement of HDPE with 20% or 40% HA particles caused a significant reduction in creep rate, however this was accompanied by a significant loss in ductility. The unfilled polyethylene samples were shown to have a creep rate that decreased with log(time) up to strains of 2%, indicating that the behaviour was still primarily viscoelastic, with no early signs of failure that would be indicated from an accelerating or tertiary creep phase. High-density polyethylene would be expected to accommodate creep strains of at least 5%, and so this is no surprise. For the filled samples, however, an acceleration of the creep rate towards failure was seen. For the 20% reinforced material, this was seen at a strain of about 1.5%, while for the 40% reinforced material this occurred with a strain as low as 0.4%. This dramatic loss of ductility was attributed to debonding of the filler particles from the matrix, which is a well-known failure mechanism for particle-filled polymers. In a further paper [24], the effects of HA reinforcement on creep behaviour in Ringer's solution were studied. It was found that Ringer's caused an increase in creep rate for the filled materials, which was not attributed to matrix plasticisation, due to the limited water absorption of polyethylene. Rather, it was caused by absorption of water at the particle/matrix interface and reduction in interfacial strength. This was supported by the fact that liquid uptake increased with the reinforced materials.

If realistic predictions of creep behaviour are to be made over the lifetime of an implant (often greater than 15 years), then extrapolations are required as it is not practical to conduct such long tests. Prediction of the creep behaviour of polymers is an extensively studied area and so the study outlined here focuses on some of the most practical and reliable methods. Probably the most widely used extrapolative method is that based on time-temperature superposition (TTS), which has been used for prediction of creep in PMMA cements [25]. By conducting tests at different temperatures, and then shifting along the time axis, a master curve can be produced allowing predictions at longer times. A similar approach is that of stress-time superposition (STS), which argues that a higher stress leads to a simple acceleration in the creep behaviour. Both of these methods rely on the assumption that the state of the material does not change with temperature, stress or time, although they do not necessarily assume linear viscoelasticity. In practice, all of these assumptions may not be valid; the properties may change with temperature due to additional curing; increases in stress may lead to localised yielding and the gradual changes associated with physical ageing will not be accommodated.

Physical ageing is the process whereby a non-equilibrium glassy structure gradually changes towards the equilibrium state through slow molecular motions. It causes an increase in density and a decrease in the creep rate. It occurs in all polymers below their glass transition temperature (T_g), including PMMA and PEMA bone cements [20, 25]. If physical ageing is neglected from creep modelling, then the predicted creep rates tend to be far higher than the actual rates, as on-going physical ageing slows the creep behaviour. The most comprehensive study of physical ageing has been given by Struik [26] who also developed a method of predicting its effects on creep via an ''effective time model''. This relies on the use of ''momentary creep curves'', where the prior ageing time is longer than the time of testing, i.e. the ageing state is effectively constant during the test. By conducting tests with different prior ageing times, a 'master curve' can be generated that allows the rate of ageing to be calculated. This then allows the calculation of the effective time of a creep test, which is the time required to achieve the same creep strain if ageing had been ongoing. When combined with TTS (or STS), this is potentially a very powerful technique.

Struik also noted that the momentary creep curves of a wide range of materials can be fitted to his ''universal creep equation'', given in Eq. (1), where $D(t)$ is the creep compliance, D_0 is the initial compliance and m and τ are constants. Struik also found that the value of m was close to 0.3 for most systems studied.

$$D(t) = D_0 \exp\left(\frac{t}{\tau}\right)^m \tag{1}$$

A more mathematical approach to the modelling of ageing was provided by Tomlins et al. [27] who replaced the time function (t/τ) used in many creep equations with an integrated time function:

$$\int_0^t \frac{du}{\tau(u)} \quad \text{where} \quad \tau^2(t) = \tau^2 + C^2 t^{2b} \tag{2}$$

with u a dummy time variable and C and b constants.

This approach can then be used with any equation describing the short-term creep, for instance, in combination with Struik's 'universal' equation (Eq. (1)), it yields Eq. (3):

$$D(t) = D_0 \exp\left[\int_0^t \frac{du}{(u)}\right]^m \tag{3}$$

Whilst in combination with the Williams–Watts [28] description of creep (Eq. (4) it yields Eq. (5). ΔD_α is a further material constant.

$$D(t) = D_0 + \Delta D_\alpha \left[1 - \exp\left(-\frac{t}{\tau}\right)^m\right] \tag{4}$$

$$D(t) = D_0 + \Delta D_\alpha \left[1 - \exp\left(-\int_0^t \frac{du}{(u)}\right)^m\right] \tag{5}$$

The potential use of each of these methods for predicting the creep behaviour of PEMA-based bone cement is presented below. The following important limitations should be noted:

- Samples were prepared using methods that would not be practicable in an operating theatre but nevertheless give reproducible material, as the study was intended to be of the material's inherent behaviour, rather than a simulation of exact service conditions.
- The work considers creep deformation alone, with no prediction of failure or fracture. With PEMA-based cements, however, it is excessive creep deformation that is likely to be far more of a problem than ultimate failure, and so this is not unreasonable.
- The study focuses more on the creep behaviour as a function of time (including effects of ageing time and gradual curing) and the effects of stress are less fully

investigated. To extend the study to a complete description of the creep behaviour, as would be required for modelling purposes, further work on the effects of stress above 2 MPa is needed.

- In addition, samples were tested in tension rather than compression or shear, and temperatures ranging from 24 to 50°C were used. The use of tension can be justified partly as tensile stresses do occur within arthroplasties and also that the effects of tension, compression and shear on creep deformation behaviour have been found to be quite similar [19].

Materials and methods

Material preparation

The constituent elements of the PEMA-based cement were a powder component containing polyethylmethacrylate and 0.6% (by weight) of a benzoyl peroxide initiator (TS 1364 from Bonar Polymers, Newton Aycliffe, Co. Durham, UK), and a liquid made up of *n*-butylmethacrylate including 2.5% by volume *N*, *N*, dimethyl-p-toluidene. The powder to liquid proportions were maintained at a 2:1 weight ratio, normally mixing 40 g of powder with 20 g of liquid. In addition, samples containing either 10% or 25% by weight of hydroxyapatite powder were produced. As an example, a 25% HA batch would contain 25 wt% of HA, 50 wt% of PEMA powder and 25 wt% butylmethacrylate. The HA (grade P81B), with a mean particle size of 3.3 μm was supplied by Plasma Biotal Ltd. (Buxton, Derbyshire, UK). The mixing procedure was kept constant throughout with the powder being added to the liquid and vigorously mixed for 60 s, before a slow 1 Hz mix until the onset of the dough stage, determined via ASTM F451-86. The resulting dough was then hand pressed into a 200 × 200 mm sheet containing twelve 70 × 40 × 3 mm test piece mould cavities. This sheet was then placed under a 750 kPa compressive stress for 30 min and the resulting specimens removed and stored at their subsequent testing temperature in an environment of buffered Ringer's solution to mimic a physiological salt solution. The use of a fat solution (such as Intralipid) was considered, but as previous work with this cement had found that Ringer's solution produced the highest creep rates, this was discounted.

Weight change measurements

The amount of water absorbed by the bone cement was measured by immersing samples in Ringer's solution at 24°C and at 37°C and periodically measuring the weight on a balance accurate to 0.1 mg. Immersion was continued until a constant weight was achieved. In order to establish the rate of monomer loss, control samples, aged in air were also measured at these temperatures, and the weight of the immersed samples was measured as they were subsequently allowed to dry in air.

Creep testing

All creep tests were performed on RAPRA designed constant load creep machines capable of testing in a variety of environments at a wide range of temperatures. For all tests, the creep deformation was continually monitored using displacement transducers with a strain resolution of 3×10^{-5}. This was then used to produce values of creep compliance (creep strain/applied stress). Good reproducibility between repeat tests was observed.

The effects of hydroxyapatite reinforcement

The weight change results are shown in Fig. 1. These show that all the samples in Ringer's solution increase in weight, due to water absorption, while all those in air lose weight, due to monomer loss. The rate of monomer loss in air is higher at 37°C than at 24°C, not surprisingly, but is also higher for the filled materials compared to the unfilled materials. This suggests incomplete curing in the filled samples, which was also seen with a decreased T_g as measured by DMTA. This important effect is most probably caused by the presence of HA filler particles either decreasing the mobility of the unreacted constituents of the bone cement or reducing the temperature reached during curing and thus preventing complete cure. The weight increases in Ringer's solution are complicated by the combined effects of water absorption and monomer loss. In order to clarify this, the samples immersed in Ringer's

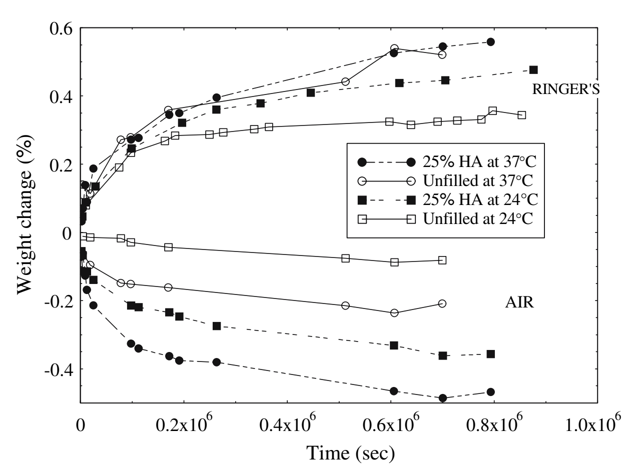

Fig. 1 The weight change of bone cement samples after immersion in Ringer's solution and conditioning in air

solution were then allowed to dry out, and this gave a measure of the monomer loss whilst immersed. Assuming the monomer loss rate to follow the same time variation as seen in air, the net water absorption could be calculated as a function of time, and this is shown in Fig. 2. This shows that the filled samples display significantly higher water uptake than the unfilled samples. This is likely to be due to absorption of water into either the hydroxyapatite particles or the interface between HA and polymer. Such an effect has also been seen with HA reinforced PE [24].

The effect of hydroxyapatite reinforcement on the creep behaviour is shown in Fig. 3, for samples tested at a stress of 1 MPa, in Ringer's solution at 37°C after an ageing time of 7 days. This shows that both the initial compliance and the creep rate are reduced by increasing amounts of HA filler. An increase in short-term stiffness was also seen with DMTA results. Recovery behaviour was also measured after 1 h of creep under the same conditions and the fractional recovery is shown in Fig. 4. This shows that the HA reinforced samples show slower and less complete recovery. This may be due to some separation of the HA particles from the polymer matrix during creep, although the creep curves show no sign of acceleration towards failure. It could also be due to continued curing whilst under stress.

A comparison of time temperature superposition and stress time superposition

In order to investigate the effectiveness of time-temperature superposition, a series of creep tests was performed on the unfilled material at temperatures of 24, 30, 37, 40, 45 and 50°C, all with a prior ageing time (at the test temperature) of 1 day and at a stress of 1 MPa. The resulting

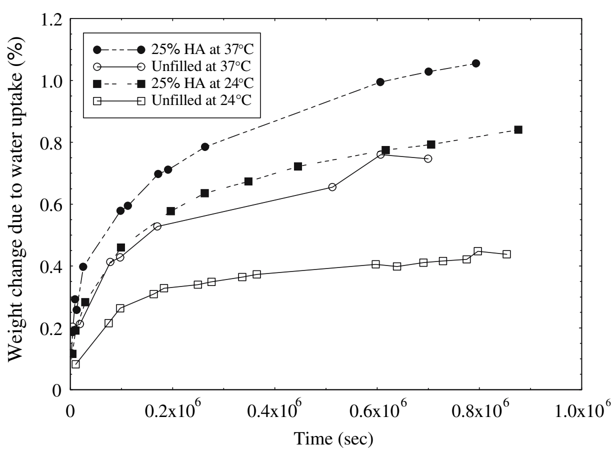

Fig. 2 The net water absorption with time, accounting for monomer loss

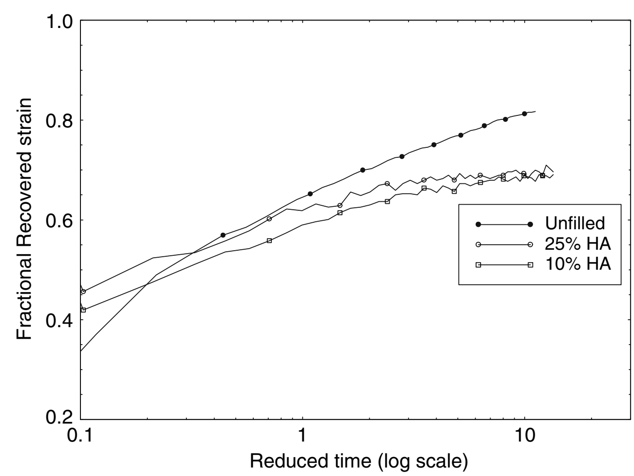

Fig. 4 Recovery behaviour after 1 h of creep under the same conditions as Fig. 3

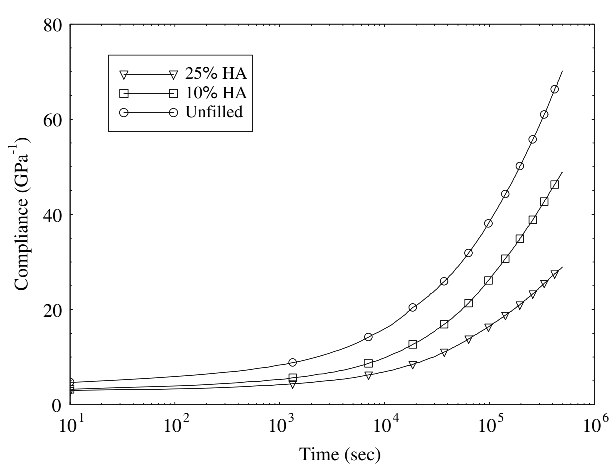

Fig. 3 The effect of hydroxyapatite filling on creep behaviour, with a stress of 1 MPa in Ringer's solution at 37°C after a 7 day ageing time

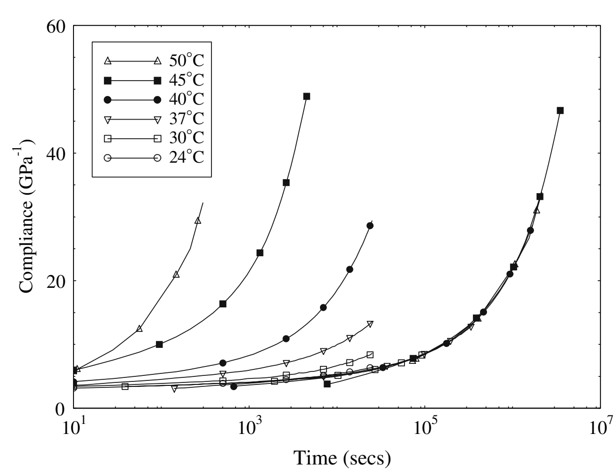

Fig. 5 Creep curves at various temperatures, with resulting master curve for unfilled bone cement at a stress of 1 MPa after 1 day ageing

creep curves are shown in Fig. 5. The creep tests were halted either when the time reached one third of the prior ageing time or when the compliance reached 50 GPa^{-1}. In order to apply the TTS method, it was necessary to shift each curve along the time axis to produce a single master curve. This was done by firstly fitting Struik's equation (Eq. (1)) to each curve, generating individual values of D_0, τ and m. It was found that the values of m were very similar in each case and an average value of 0.276 was used for all curves. The values of D_0 and τ obtained are given in Table 1. In order to produce a master curve at 24°C, the other curves were fitted to Eq. (1) using the 24°C constant values, along with a shift factor a, as given in Eq. (6).

$$D(t) = 2.978\ \exp\left(\frac{t.a}{86142}\right)^{0.276} \tag{6}$$

These shifted curves superpose with a good deal of accuracy involving no vertical shifts and form a consistent master curve, also shown in Fig. 5. There are slight discrepancies with the very short time data of each test, but this is probably just due to strain fluctuations shortly after loading.

The shift factors are plotted against temperature in Fig. 6. These data can be compared to the WLF equation (Eq. (7)), often used for such superpositioning, where T is the test temperature, T_s the reference temperature and C_1 and C_2 are constants. Figure 6 shows that this can provide a good fit to the experimental data (R^2 = 0.96).

$$\log a = \frac{C_1(T - T_s)}{C_2 + T - T_s} \tag{7}$$

Similar superposition was performed with the 10% and 25% HA reinforced materials, with a similar degree of success. In these cases, the lowest temperature used was 37°C, and this was used as the reference temperature. The data and master curve for the 25% HA reinforced samples are shown in Fig. 7. It is encouraging that the TTS method can account for creep deformation at different temperatures, even though there may be differences in delayed curing, especially with the reinforced materials.

Stress-time superposition can also be used to extrapolate creep behaviour. This was investigated with these materials, but found not to be successful, mainly as the shape of the creep curves changed with increasing stress. This can be seen in Fig. 8, where the creep compliance is plotted for stresses between 1 and 8 MPa for the unfilled material. This shows that the material can be considered linearly viscoelastic (stress independent) up to 2 MPa, but becomes non-linear above this. As the effects of stress are non-linear, the foregoing creep predictions are only strictly applicable to the stress used, namely 1 MPa, and possibly up to 2 MPa. In order to extend the results presented in this paper to a more general creep model, able to accommodate a wider range of stresses, further work would be needed to

Table 1 The values of D_0 and τ used for time-temperature superposition for unfilled bone cement

Temperature (°C)	D_0 (GPa^{-1})	τ (s)
24	2.978	86,142
30	3.016	22,796
37	3.330	7,304.7
40	3.436	1,549.9
45	4.252	176.5
50	3.280	8.768

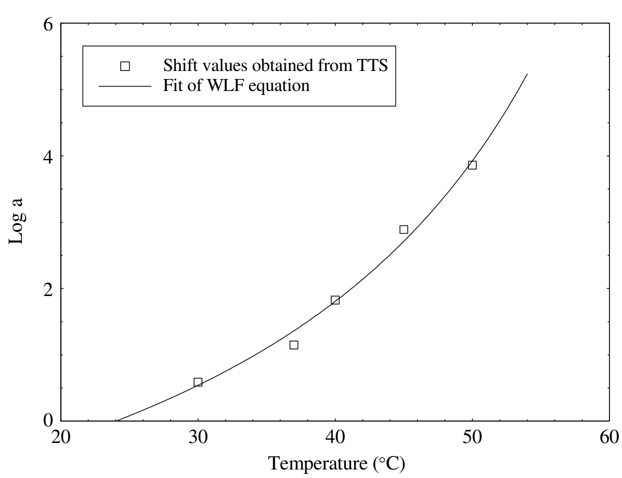

Fig. 6 Shift factors used to generate the master curve in Fig. 5

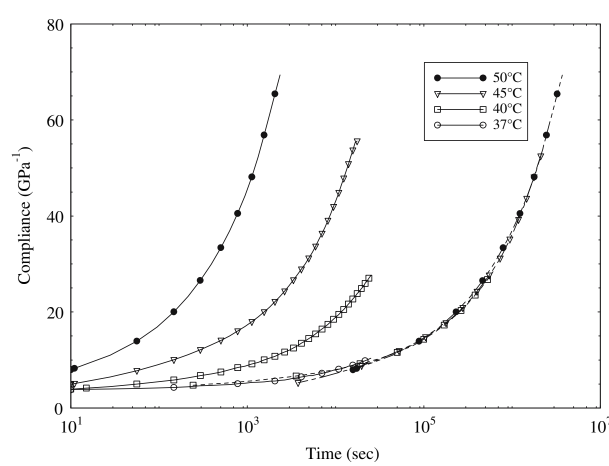

Fig. 7 Creep curves at various temperatures, with resulting master curve for 25% HA filled bone cement at a stress of 1 MPa after 1 day ageing

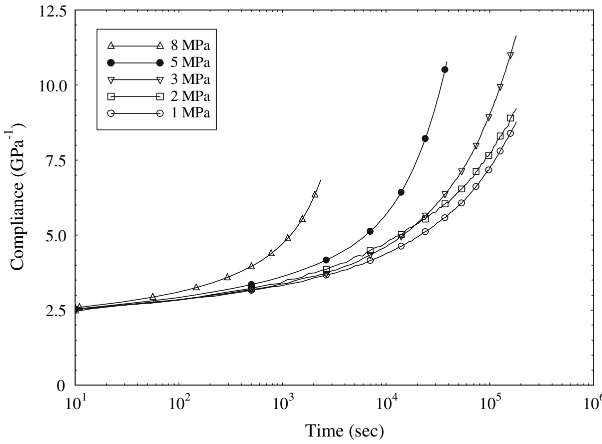

Fig. 8 Creep compliance versus time for unfilled bone cement at various stresses, at a temperature of 37°C after 1 day ageing

establish the exact influence of higher stresses on creep deformation.

Creep prediction using effective time

Although TTS seems quite successful, this method takes no account of any on-going physical ageing, and so although the TTS master curve (Figs. 5, 7) predicts the creep compliance up to 40 days, significant ageing will be occurring from 1 day and so the prediction will be a significant overestimate of the compliance.

In order to assess Struik's effective time method of accounting for ageing, a set of short-term creep tests was required with different prior ageing times. The approach adopted was similar to Struik's, using a test regime of creep and recovery with single samples. This has the advantage that sample to sample variability is reduced, but it does mean that the extrapolation of recovery must be subtracted from the subsequent creep behaviour. Duplicate samples were tested to ensure representative results. Figure 9 shows the resulting creep compliance for the unfilled material, tested at 37°C at a stress of 1 MPa for ageing times (t_e) of 3–720 h. The dashed lines in Fig. 9 represent the best fits of Struik's creep equation to the data, with a fixed value of m equal to 0.245. The curves at different ageing times were then shifted along the time axis to produce a very good master curve, shown in Fig. 10. According to the effective time theory, the variation of shift factor with ageing time should be linear on a log-log plot, with a gradient of between 0.7 and 1. This is shown to be the case in Fig. 10, with a gradient, termed the ageing rate (μ) equal to 0.78.

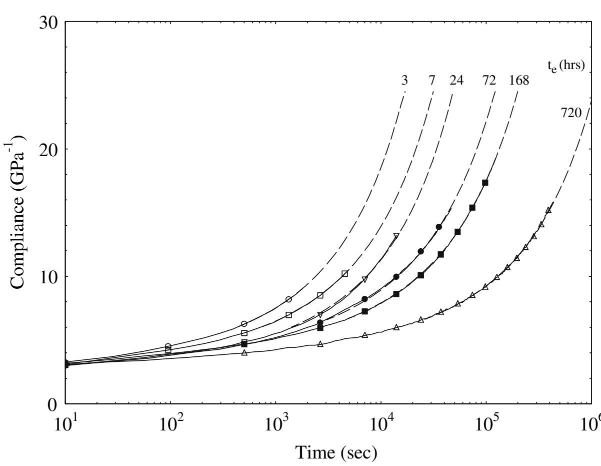

Fig. 9 Creep curves after various ageing times for unfilled bone cement at a stress of 1 MPa and a temperature of 37°C

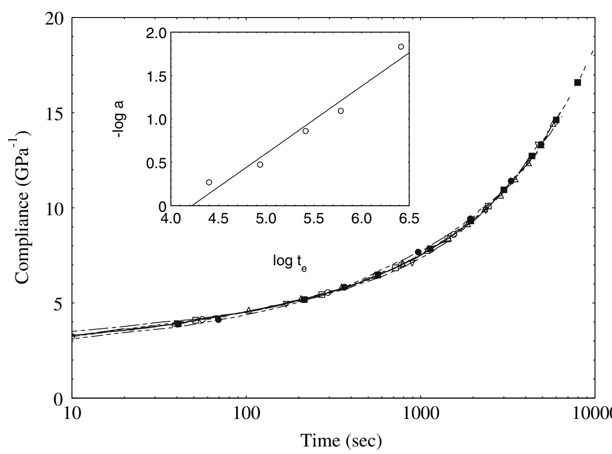

Fig. 10 The master curve and shift factors for the tests at various ageing times shown in Fig. 9

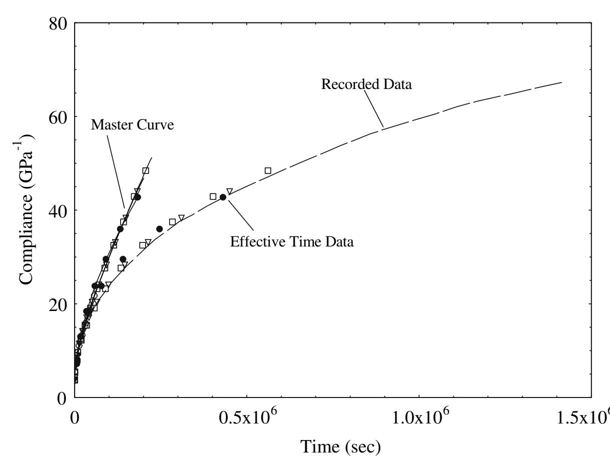

Fig. 11 The master curve generated from TTS, along with the effective time data and long-term experimental data for creep of unfilled bone cement at 1 MPa, 37°C and 1 day prior ageing

Once the shift rate had been calculated, the next step was to create a longer time momentary creep curve, which can only be done through a superposition technique; TTS in this case. This was done in the same manner as described above, except that in this case a master curve at 37°C was required rather than at 24°C. This is shown in Fig. 11, plotted on a linear timescale. In order to include the effects of ageing into this master curve, Eq. (8) was used to convert the time of any point on the momentary master curve into the effective time.

$$\lambda = t_e \left[\left(\frac{t_c.\alpha}{t_e} + 1 \right)^{1/\alpha} - 1 \right] \tag{8}$$

Where λ is the effective time, t_c the recorded creep time, t_e the prior ageing time, and α equal to $(1-\mu)$. The momentary master curve was then re-plotted using the effective time rather than the creep time and this is also shown in Fig. 11. In addition, a long-term test was conducted under the same conditions and this is shown as the dashed line in Fig. 11. It can be seen that had the master curve been used taking no account of ageing, a large overestimate in creep would have occurred, whereas the effective time data fit the observed long-term data very well. The degree of extrapolation is not especially large in this case, due to the creep tests rapidly reaching the maximum measurable compliance in the higher temperature tests.

Similar analyses have been performed for material filled with 10% and 25% of hydroxyapatite and show a good prediction of the long-term experimental data, with a possible extrapolation of 20 times.

Creep prediction using integrated time

Although the use of effective time seems to be a very successful way of accounting for ageing and hence predicting long-term creep, it is quite a complex method that requires considerable testing. The following section explores the extent to which integrated time equations can be used to simplify the creep prediction process. An analysis was performed using both the Struik equation (Eq. (1)) and the Williams–Watts equation (Eq. (4)). The first stage in each of these cases is to generate a momentary creep curve, where ageing is insignificant. In this case, tests conducted at 37°C at a stress of 1 MPa and a prior ageing time of 1 day were used. The data was then fitted to Eqs. (1) or (4) to generate values of D_0, τ, m and ΔD_α which are given in Table 2.

The second step was to use a long-term creep test (where ageing is significant) to generate values for C and b as used in the integrated time function (Eqs. (3), (5)). In order to do this, the data were re-plotted in the form:

$$F(D(t)) = \frac{t}{\tau(t)} \tag{9}$$

using an appropriate $F(D(t))$ for either the Struik or Williams–Watts equation. The gradient of the subsequent plot gave the variation of $\tau(t)$, from which the constants C and b could be determined using Eq. (2). The values of C and b (shown in Table 3) were found by fitting the first 300,000 s of the long-term creep curves, thereby allowing a test of the prediction methods using the longer data. Having obtained values of D_0, τ, m, C, b and ΔD_α (if

Table 2 The fitting parameters used for momentary creep curves

		D_0 (GPa^{-1})	τ (s)	m	ΔD_α (GPa^{-1})
Unfilled	Struik	2.558	2,097	0.245	–
	Williams–Watts	3.900	8.00×10^7	0.601	400
10% HA	Struik	2.480	2,836	0.247	–
	Williams–Watts	3.391	2.08×10^7	0.521	350
25% HA	Struik	2.707	10,885	0.292	–
	Williams–Watts	3.052	2.889×10^7	0.511	250

Table 3 The parameters used for the integrated time function

		C	b
Unfilled	Struik	0.240	0.817
	Williams–Watts	2820	0.674
10% HA	Struik	0.107	0.890
	Williams–Watts	328.6	0.825
25% HA	Struik	0.126	1.001
	Williams–Watts	468.9	0.875

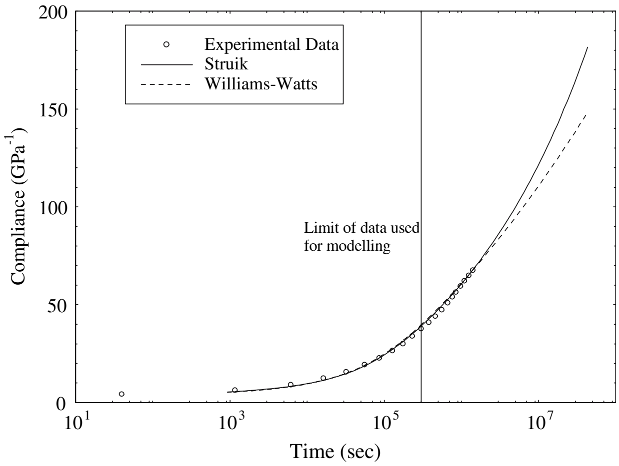

Fig. 12 Comparison of long-term creep data with predictions using integrated time functions for unfilled bone cement at 1 MPa, 37°C and 1 day prior ageing

needed) it is possible to construct predictive curves that can be compared to long-term data. These comparisons are shown in Figs. 12, 13, 14 for the unfilled, 10% HA and 25% HA materials respectively. It can be seen that the predictions of both equations are generally very good. The Williams–Watts equation predicts a lower creep rate at longer times, and there is some evidence from the 10% HA material that this is the more representative behaviour. Despite this, the use of either form will not lead to significant errors in creep prediction. The degree of extrapolation between the 300,000 s used for modelling and the measured data is less for the unfilled material at 4.5 times, and greater for the filled materials at 13 times. This again reflects the fact that creep measurements for the unfilled material were limited by the large compliances observed. Given the good fits, it is likely that extrapolations of at least 20 times can be made with reasonable confidence.

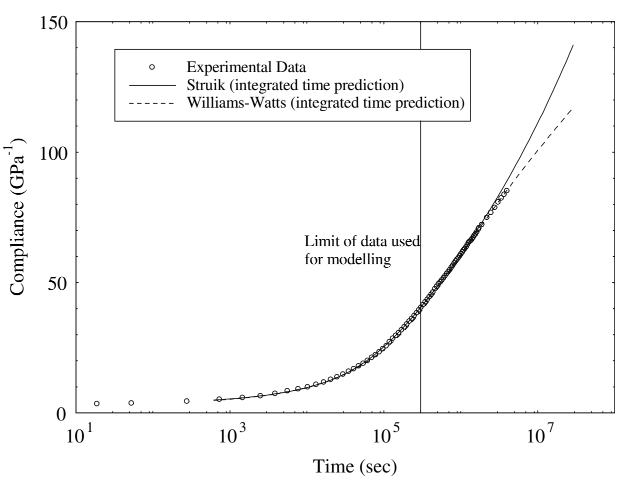

Fig. 13 As Fig. 12, for bone cement filled with 10% hydroxyapatite

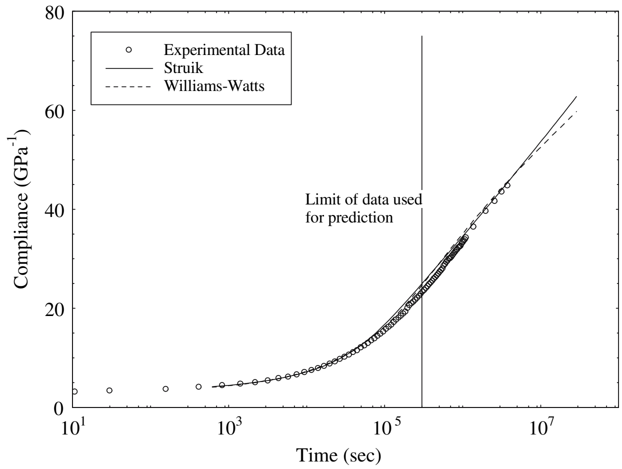

Fig. 14 As Fig. 12, for bone cement filled with 25% hydroxyapatite

It should also be noted that the longest experimental data for the filled material shows no sign of acceleration, which would indicate a failure mechanism such as extensive particle debonding. This is despite the creep strains reaching over 8% for the 10% HA material and over 5% for the 25% HA material.

Conclusions

Reinforcement of PEMA based bone cement with hydroxyapatite particles seems to be an effective method of reducing the creep rate. Reinforcement with 25% of HA resulted in a 25% increase in short term stiffness, but the creep compliance at 10^7 s is reliably predicted to be less than half that of the unfilled material. Despite this, there do seem to be some drawbacks with the incorporation of HA particles. There is clear evidence of less complete curing, probably due to the HA particles hindering molecular motion or reducing temperatures during curing. This leads to increased monomer loss compared to unfilled material. Greater water absorption is also seen with the filled materials, either due to water absorption into the HA particles or at the interfaces. The degree of recovery is also less complete with HA reinforcement. These issues would need to be addressed at least partially if this approach to reducing creep in PEMA bone cements is to be effective.

A study of creep prediction methods has shown that the use of Stress Time Superposition is unreliable due to the material's non-linear behaviour at higher stresses. Time Temperature Superposition seems to be much more effective, allowing a longer timescale master curve to be generated. Importantly, this method on its own takes no account of ongoing physical ageing and will lead to a dramatic overestimate of creep compliance at longer times.

The effects of ageing can be dealt with by either the effective time approach, or by the use of integrated time functions. Both give reliable correlations with the long-term data, measured to a time of 46 days. The degree of extrapolation possible using the effective time approach is limited by the maximum compliance that can be measured during short-term elevated temperature tests. For the integrated time approach, the potential extrapolation is boundless, and so is only limited by the confidence in the method. It is likely that extrapolations of at least 20 times are reasonable.

The effective time method has a requirement for more experimental testing, with 9 tests of up to 10^5 s required in this case for a reasonable prediction. The number of tests required for the integrated time approach is less, being possible with a single test, the first part of which is treated as a short-term test (with no ageing) and the latter part as a long-term test (with ageing). The amount of data required for this test is however larger, with tests needing to be run to 3×10^5 s for good predictions. Despite this, the integrated time approach is probably the most practical and reliable method of creep prediction with these materials. Although there is little difference between the predictions of the Struik or Williams–Watts equations, the latter is probably more accurate.

There is no evidence of the early signs of creep failure from these tests, even though creep strains exceeded 5% in all cases and were up to 8% for one material. This indicates that even with HA filled PEMA bone cements, excessive creep deformation is still likely to be more of a problem than creep fracture.

References

1. P. HERBERTS, J. KARRHOLM and G. GARELLICK, Annual Report 2004, The Swedish National Hip Arthroplasty Register, The Swedish National Hip Arthroplasty Register, Goteburg, (2004)
2. T. A. GRUEN, G. M. MCNEICE and H. C. AMSTUTZ, *Clin. Orthop. Relat. Res.* **141** (1979) 17
3. D. K. COLLIS, *J. Bone Joint Surg. Am.* **73a** (1991) 593
4. J. H. BOSS, I. SHAJRAWI, S. DEKEL and D. G. MENDES, *J. Biomater. Sci. Polym. Ed.* **5** (1993) 221
5. G. LEWIS, *J Biomed. Mater. Res.* **38** (1997) 155
6. N. VERDONSCHOT and R. HUISKES, *J. Bone Joint Surg.* **79B** (1997) 665
7. K. W. M. DAVY and M. BRADEN, *Biomaterials* **12** (1991) 540
8. B. WEIGHTMAN, M. A. R. FREEMAN, P. A. REVELL, M. BRADEN, B. E. J. ALBREKTSSON and L. V. CARLSON, *J. Bone Joint Surg.* **69** (1987) 558
9. G. M. BRAUER, D. R. STEINBERGER and J. W. STANSBURY, *J. Biomed. Mater. Res.* **20** (1986) 839
10. C. LUI, S. M. GREEN, N. D. WATKINS, P. J. GREGG and A. W. MCCASKIE, *J. Mater. Sci. Mater. Med* **13** (2002) 1021
11. N. VERDONSCHOT and R. HUISKES, *J. Biomed. Mater. Res.* **53** (2000) 498
12. D. N. YETKINLER and A. S. LITSKY, *Biomaterials* **19** (1998) 1551
13. N. VERDONSCHOT and R. HUISKES, *J. Biomed. Mater. Res.* **28** (1995) 575
14. T. L. NORMAN, V. KISH, J. D. BLAHA, T. A. GRUEN and K. HUSTOSKY, *J. Biomed. Mater. Res.* **29** (1995) 495
15. J. P. G. WHEELER, A. W. MILES and S. E. CLIFT, *Mater. Sci. Mater. Med.* **10** (1999) 497
16. C. LUI, S. M. GREEN, N. D. WATKINS, P. J. GREGG, A. W. MCCASKIE, *J. Mater. Sci. Lett.* **21** (2002) 959
17. R. D. CROWNINSHIELD, R. A. BRAND, R. C. JOHNSON and J. C. MILROY, *J. Bone Joint. Surg.* **62A** (1980) 68
18. R. De SANTIS, F. MOLLICA, L. AMBROSIA, L. NICOLAIS and D. RONCA, *J. Mater. Sci. Mater. Med.* **14** (2003) 583
19. A. J. C. LEE, R. S. M. LING, S. GHEDUZZI, J. P. SIMON and R. J. RENFRO, *J. Mater. Sci. Mater. Med.* **13** (2002) 723
20. J. C. ARNOLD and N. P. VENDITTI, *J. Mater. Sci. Mater. Med.* **12** (2001) 707
21. K. SERBETCI, F. KORKUSUZ and N. HASIRCI, *Polymer Testing* **23** (2004) 145
22. E. J. HARPER, J. C. BEHIRI and W. BONFIELD, *J. Mater. Sci. Mater. Med.* **6** (1995) 799
23. J. SUWANPRATEEB, K. E. TANNER, S. TURNER and W. BONFIELD, *J. Mater. Sci. Mater. Med.* **6** (1995) 804
24. J. SUWANPRATEEB, K. E. TANNER, S. TURNER and W. BONFIELD, *J. Mater. Sci. Mater. Med.* **8** (1997) 496.
25. R. L. MORGAN, D. F. FARRAR, J. ROSE, H. FORSTER and I. MORGAN, *J. Mater. Sci. Mater. Med.* **14** (2003) 321
26. L. C. E. STRUIK, *Physical aging in amorphous polymers and other materials*. Elsevier, Amsterdam (1978)
27. P. E. TOMLINS, B. E. READ and G. D. DEAN, *Polymer* **35** (1994) 4376
28. G. WILLIAMS and D. C. WATTS, *Trans. Farad. Soc.* **66** (1970) 80