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Creep behavior of bone cement: a method for time extrapolation using time-temperature equivalence

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The clinical lifetime of poly(methyl methacrylate) (PMMA) bone cement is considerably longer than the time over which it is convenient to perform creep testing. Consequently, it is desirable to be able to predict the long term creep behavior of bone cement from the results of short term testing. A simple method is described for prediction of long term creep using the principle of time–temperature equivalence in polymers. The use of the method is illustrated using a commercial acrylic bone cement. A creep strain of approximately 0.6% is predicted after 400 days under a constant flexural stress of 2 MPa. The temperature range and stress levels over which it is appropriate to perform testing are described. Finally, the effects of physical aging on the accuracy of the method are discussed and creep data from aged cement are reported.

1. Introduction

Poly(methyl methacrylate) (PMMA) bone cement was introduced in the 1950s, mainly through the work of Charnley [1]. It is still widely used in orthopaedic surgery and is used primarily as an intermediate load bearing implant material between prosthesis and bone. The success of a cemented implant depends, in part, on the mechanical performance of the cement. Both the bulk properties and the interfacial properties of the cement are important. It is required to sustain loads under a variety of geometries and over a wide range of time scales. Consequently, there is an extensive body of literature documenting the mechanical properties of acrylic cement. The fatigue, fracture, creep, relaxation and quasistatic properties have all been characterized; for a review see Lewis [2].

Bone cement is required to sustain loads over long time periods and, in common with other viscoelastic materials, it undergoes creep. The creep properties of a bone cement therefore require characterization. The clinical effect of the creep of bone cement is not, however, well understood. Creep has been implicated in prosthesis subsidence [2], in particular subsidence of the femoral stem in hip replacement. Excessive subsidence can lead to prostheses loosening, which, in turn, can lead to pain and to increased osteolysis. However, it has also been postulated that a limited degree of creep may help in maintaining the cement–implant interface [3].

Creep studies have been performed both in compression [4–6] and in tension [7], for durations up to 100 h. Creep strains of up to 1% at physiological stress levels have been measured over these relatively short time scales. Since cemented arthroplasties have a typical lifetime of more than 15 years it would be expedient to be able to predict the creep behavior of bone cement over a period of years. In this paper we introduce a method which allows the prediction of long time creep behavior, through the extrapolation of short time creep data. The method represents an alternative to fitting an empirical model to short term data and extrapolating as a function of time [4].

The extrapolation method is based on the observation that the viscoelastic behavior of polymers can display time–temperature equivalence [8]. In its simplest form, the equivalence means that the viscoelastic behavior at one temperature can be related to the behavior at another temperature through a shift in the time scale. We shall refer to this as the time–temperature superposition principle (TTSP). The TTSP can be used to obtain viscoelastic properties over a wide range of either time or frequency. The way in which we have applied the TTSP is to collect data in the form of creep strain versus time at a series of different temperatures at, and above, physiological temperature (37 °C). These data are then extrapolated as a function of time, at 37 °C, by shifting the data collected at the different temperatures. A temperature dependent shift factor is calculated using an appropriate relationship.

In this paper we assess the use of the TTSP to predict the long term creep performance of bone cement. A single commercial bone cement is used throughout. The loading geometry we have used is flexure but we believe the findings of the paper to be equally valid for other geometries. The details of the extrapolation method are described and its limitations are discussed.

2. Materials and methods

2.1. Materials

Testing was performed on a commercial acrylic cement. The identity of the cement is not disclosed since the purpose of this paper is solely the assessment of a method and it is not an evaluation of the properties of a specific bone cement. Consequently we shall refer to the material simply as cement A. The cement is prepared using methyl methacrylate monomer and methyl methacrylate-methylacrylate copolymer powder, with zirconium dioxide as a radiopacifier.

Samples were prepared by curing in a mold for 25 min at 37 °C, under a force of 50 kN. The test pieces had approximate dimensions of 50 × 2 × 7 mm. The samples were aged for 1 week at 37 °C and then stored at room temperature prior to testing, unless otherwise stated.

2.2. Mechanical testing

All mechanical testings were performed on a dynamic mechanical thermal analyzer (DMTA) under dry conditions. The instrument was a Rheometrics Solid Analyzer RSAII. Measurements were made using a three point bending geometry and a span length of 48 mm.

Creep testing was performed using a constant static force. The magnitude of the force was selected in the following manner. The strains experienced by bone cement when set around a prosthesis have been measured experimentally during loading of the prosthesis [9]. We used these results, and an applied force equal to body weight, to calculate a suitable stress for simulating the constant long term stresses experienced by bone cement. We are aware that forces higher than body weight are experienced by cement, for example during a walking cycle, but these are momentary forces and are not of primary importance to the investigation of long term creep. In order to simplify our experiments we selected stress levels that would lead to linear viscoelastic behavior. A stress level of 2 MPa was selected at 37 °C. At higher temperatures creep tests were performed both at 2 MPa, and a lower stress of 1 MPa, in order to ensure that conditions of linear viscoelasticity were achieved. Test times of typically 6 h were employed, with measurements of displacement recorded at 30 s intervals. The creep data collected in each test were processed to yield plots of creep compliance (creep strain divided by stress) versus time to allow comparison of data recorded at differing stress levels. Testing was performed on cement A at the following temperatures: 21, 37, 47, 57 and 67 °C. The range of test temperatures appropriate for use in the time extrapolation was selected using a plot of mechanical properties as a function of temperature.

The thermal mechanical properties of the cement were determined over the temperature range 5–90 °C in order to identify a suitable temperature range for the extrapolation method. Dynamic bending tests were performed at a frequency of 1 Hz, with a strain of approximately 0.4%. A constant static force was applied to maintain flexure during the dynamic cycle. The applied dynamic force was varied to achieve approximately constant strain as a function of temperature and the static force was varied accordingly. The heating rate was 2 °C/min.

2.3. Time–temperature extrapolation

The simplest form of the TTSP implies that the viscoelastic behavior of a polymer at different temperatures can be related through a shift only in time scale. When applied to creep, the principle is used to produce a single creep compliance curve, on a logarithmic time scale, by selecting a reference temperature and applying a horizontal shift to the data collected at other temperatures so that these superimpose with the data collected at the reference temperature. The aim is to shift the different curves so that they superimpose as closely as possible. The superimposed curve is then assumed to represent the true viscoelastic behavior of the material at that reference temperature. In our case the reference temperature is 37 °C. The shift factor is temperature dependent and is selected in order to achieve the closest superposition. It has been suggested that a vertical shift factor should also be applied to take into account the variation in the elastic compliance with temperature [8], however, this additional factor is usually small in comparison with the horizontal factor and is usually ignored [10]. We have chosen to adopt the simpler method and use only the horizontal shift factor. The shift factor, a_T, is given by the Williams–Landel–Ferry (WLF) equation [11].

$$\log(a_T) = \frac{C_1(T - T_s)}{C_2 + (T - T_s)} \tag{1}$$

where T is the test temperature, T_s is the reference temperature, and C_1 and C_2 are constants.

The constants C_1 and C_2 are varied to give a best fit of the superimposed data.

2.4. Differential scanning calorimetry

Differential scanning calorimetry was used to measure the glass transition temperature of the bone cement. A Perkin Elmer DSC7 was used with a heating rate of 2 °C/min. The sample was heated to 170 °C and cooled to room temperature, in order to obtain improved thermal contact between sample and pan, before measuring the glass transition temperature.

3. Results and discussion

3.1. Time–temperature extrapolation

Creep testing was performed over the temperature range 21–67 °C to provide data for the extrapolation of long term creep behavior at 37 °C. Fig. 1 shows the creep compliance curves obtained from cement A. The degree

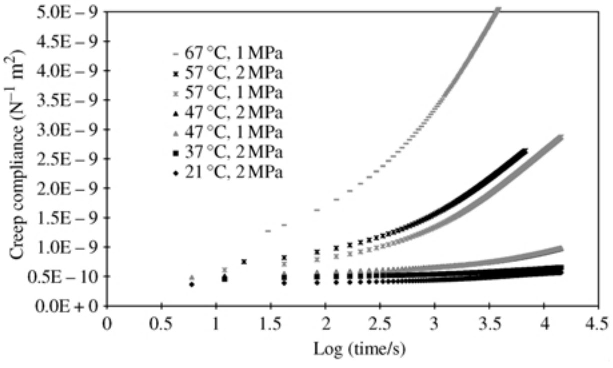

Figure 1 Plots of flexural creep compliance versus time for cement A. The curves were obtained at the temperatures and stresses indicated.

of creep can be seen to increase progressively with increasing temperature. At 47 and 57 °C compliance curves were obtained at two different stress levels. The agreement between the curves recorded at 1 and 2 MPa is sufficient for the behavior of the cement to be considered linearly viscoelastic.

The selection of appropriate test temperatures is an important component of our extrapolation method. For example it would be inappropriate to use data collected at temperatures above the glass transition in the time extrapolation of the viscoelastic behavior of a glassy material. We have made our selection using the results of a dynamic mechanical temperature sweep experiment. The temperature sweep was performed using the same testing equipment as used in the creep testing. Fig. 2 shows elastic modulus, E', and loss modulus, E'', plotted over a temperature range spanning the creep test temperatures: 5–85 °C.

Two thermal transitions are revealed by the temperature sweep. The transitions appear as peaks in the loss modulus trace: a broad peak centered at 17 °C and a sharper peak at 71 °C. Structural assignment of the transitions can be made via comparison with PMMA, which is the major component of cement A. PMMA exhibits four relaxation processes [10] and, as is customary for polymers, these are labeled in alphabetical order with decreasing temperature. The highest temperature relaxation, α, is the glass transition. In cement A the glass transition can be associated with the peak in the E'' curve at 71 °C and the slope change in the E' curve, which starts at approximately 55 °C. The peak in the E'' curve occurs close to the onset of the glass transition [12] and so does not provide a value for the glass transition temperature.* The next highest temperature relaxation, β, occurs at approximately 10 °C in PMMA and is associated with side chain motions of the ester group. The broad peak in E'' at 17 °C can clearly be assigned to a β relaxation. The two further relaxations displayed by PMMA: γ and δ, which are associated with the motion of methyl groups attached to the main chain and to side chain respectively, were not detected in the present study.

In order to select the test temperatures for use in the extrapolation method it is necessary to revisit the theoretical basis of the method. The TTSP implies that the viscoelastic behavior of a material at one temperature can be related to the behavior at another temperature through a shift in time scale. The relationship is defined by the temperature dependence of the shift factor given in Equation 1. Inspection of Equation 1 shows the shift factor to vary monotonically with temperature above its asymptotic temperature value of $T_s - C_2$. It is therefore necessary that the viscoelastic behavior should vary monotonically with temperature over the range of temperatures used in the extrapolation. We believe the appropriate temperature range to be that between the glass transition and the β transition. In the present case we have selected the data obtained at 37 and 47 °C, which lie below the glass transition onset, and 57 °C, which lies at the glass transition onset, to be used for extrapolation of creep behavior at 37 °C. The data collected at 67 and 21 °C are therefore omitted.

The time–temperature extrapolated creep behavior of cement A is shown in Fig. 3. Creep data collected at 37, 47 and 57 °C have been shifted as a function of time to form a single curve. The constants C_1 and C_2 in Equation 1 were varied in order to obtain a best fit. The choice of values for the constants and the sensitivity of the fitting to these values is discussed below. The same data are plotted in Fig. 4 as creep strain versus linear time. The

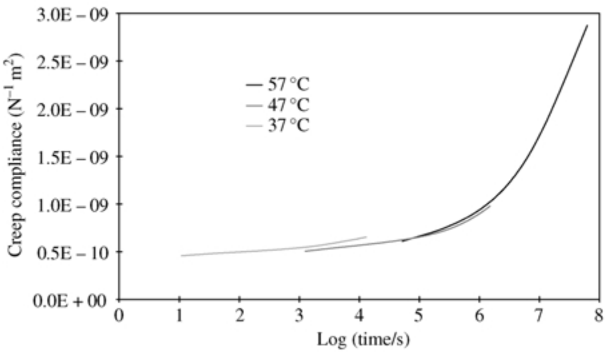

Figure 3 Time–temperature extrapolated creep compliance at 37 °C under an applied stress of 2 MPa. The fitting parameters were: $C_1 = 17.4$ and $C_2 = 75$ K. The experimental temperatures corresponding to each curve are indicated.

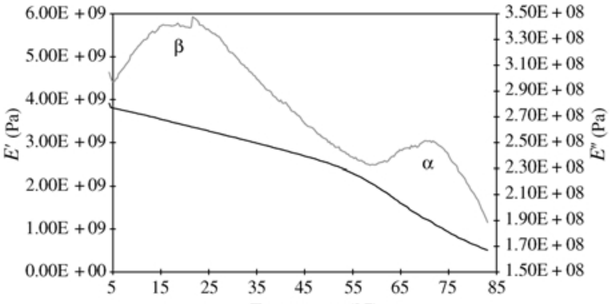

Figure 2 A plot of elastic modulus, E' (black curve), and loss modulus, E'' (grey curve), versus temperature for cement A. The two peaks in the E'' curve are assigned to the α and β relaxation processes, as shown. The change in slope of the E' curve at approximately 55 °C marks the onset of the glass transition.

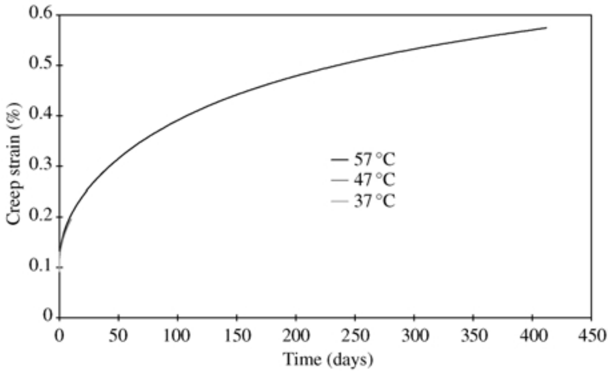

Figure 4 Time–temperature extrapolated creep strain at 37 °C under an applied stress of 2 MPa. The fitting parameters were: $C_1 = 17.4$ and $C_2 = 75$ K. The experimental temperatures corresponding to each curve are indicated.

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* The temperature sweep allowed the onset of the glass transition to be characterized through the mechanical response of the material. We were not able to record the full transition and so a value for the glass transition could not be determined by this method. The glass transition temperature was, instead, measured by differential scanning calorimetry. A value of 101.0 °C was obtained using a heating rate of 2 °C min^{-1}.

prediction extends to a time scale of 1–2 years. We realize that additional data, recorded at intermediate temperatures, would enhance the accuracy of the creep extrapolation. However, the purpose of this present paper is simply to propose a test method and discuss is validity. A creep strain of 0.57% is predicted after 400 days under a constant stress of 2 MPa.

3.2. Effect of the fitting constants: C_1 and C_2

The WLF equation, shown as Equation 1, is often written with the glass transition temperature as the reference temperature. It has been shown that this form of the equation predicts the behavior of many different polymers when the fitting constants C_1 and C_2 take universal values of 17.4 and 51.6 K. In our case the reference temperature, 37 °C, is below the glass transition temperature. We obtained a best fit by setting $C_1 = 17.4$ (the universal value) and by allowing C_2 to vary. Fig. 5 shows shifted creep curves for three different values of C_2. The data obtained at 67 °C, excluded from the creep prediction reported above, are included to allow clearer visualization of the effect of varying the fitting constants.

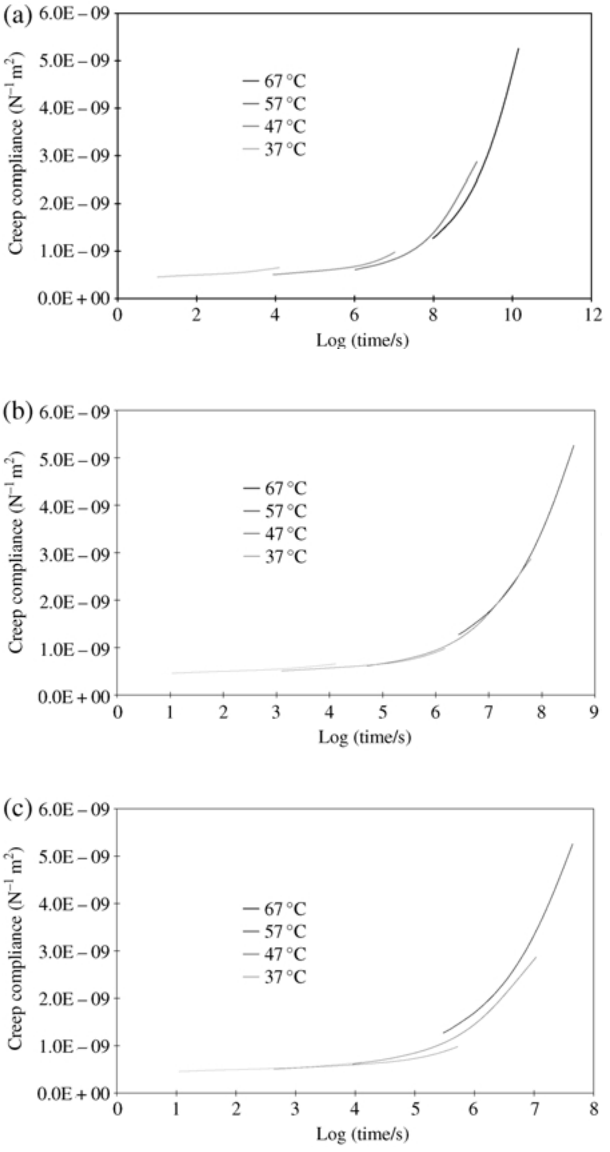

Figure 5 Time–temperature extrapolated creep compliance at 37 °C under an applied stress of 2 MPa. The experimental temperatures corresponding to each curve are marked. The plots were constructed using the following fitting parameters: (a) $C_1 = 17.4$, $C_2 = 50$ K, (b) $C_1 = 17.4$, $C_2 = 75$ K, (c) $C_1 = 17.4$, $C_2 = 100$ K.

3.3. Effects of physical aging

We have shown that the TTSP can be applied to creep data collected from a bone cement. Creep curves collected at different temperatures can be shifted to form a single curve, with reasonably smooth overlap, at a reference temperature of 37 °C. In doing so, we have taken care to use a temperature range over which the physical state of the material remains constant. A necessary assumption in this method is that the physical structure of the cement also remains constant with time. Acrylic bone cement is a glassy, amorphous polymer under physiological conditions. Like all glassy polymers it is liable therefore to exhibit slow changes in properties with time: the phenomenon known as physical aging. Physical aging occurs, for example, when amorphous polymers are cooled below the glass transition, because they do not initially reach a state of equilibrium. Equilibrium is only reached through the slow process of macromolecular rearrangement, leading to a reduction in free volume. The normal effects of aging on mechanical properties are an increase in tensile modulus and yield stress and a decrease in fracture toughness and impact strength. The polymer becomes more glassy as it ages and consequently is less prone to creep. The rate of aging is known to be a function of temperature: at temperatures just below T_g aging is rapid and at temperatures close to the beta transition aging is very slow [13].

The significance of physical aging to the application of a time–temperature extrapolation method to acrylic bone cement must be considered. If significant aging were to occur at 37 °C during the prediction time, but were not to occur during the short term tests, then the predicted creep would be over estimated. Alternatively, if little aging were to occur during the prediction time, but significant aging were to occur during the short term tests at elevated temperatures, then the predicted creep would be under estimated. In order to explore these issues we performed creep tests on samples which had been aged for 15 months at room temperature. Fig. 6 shows the original

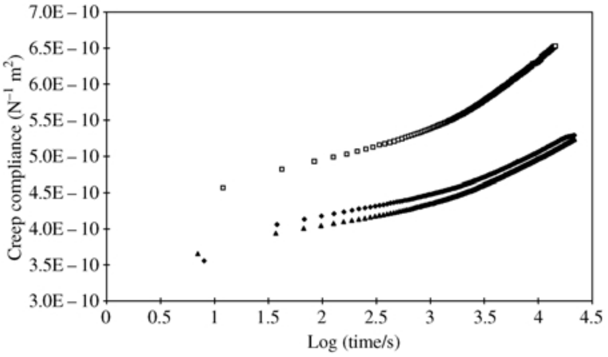

Figure 6 Plots of creep compliance versus time, recorded at 37 °C, for one sample aged at 37 °C for 1 week (open symbols) and two samples aged at 37 °C for 1 week and then 15 months at 23 °C (filled symbols).

37 °C creep data (aged for 1 week at 37 °C) alongside two additional sets of 37 °C creep data (aged for 1 week at 37 °C, followed by 15 months at room temperature). The creep behavior of the two samples aged for 15 months clearly differ from the sample aged for one week. Both the elastic response and the rate of creep of the longer aged samples are lower than those of the shorter aged material. We can infer that the bone cement has aged during 15 months storage at room temperature.

At present, we do not have sufficient data to determine the full importance of aging to our extrapolated test method. The method does not take account of physical aging and so results obtained using these methods can only be considered as a first approximation to long term creep behavior. Methods which do take account of aging are described by Struik [13] and could be used to provide an accurate prediction of long term creep behavior using short term tests. The methods are, however, considerably more involved than the simple method described as they necessitate a characterization of the aging properties as well as the time–temperature equivalence. We believe the simple method is suitable for the investigation of the comparative creep behavior of bone cements, using standardized preparation and aging conditions.

3.4. *In vivo* environment

Creep data were collected using the time–temperature superposition method under dry conditions. However, bone cement functions *in vivo* in a wet environment containing body fluids and these fluids will affect the mechanical properties of the cement. Creep data of greater clinical relevance could be generated by using the extrapolation method combined with wet testing conditions. More work is required to assess the effect of body fluids on the long term creep of bone cement.

4. Conclusions

The TTSP has been used to extrapolate the creep behavior of a PMMA bone cement.

Creep curves collected at different temperatures have been shifted to form a single curve, with reasonably smooth overlap, at a reference temperature of 37 °C. The temperatures were restricted to those between the glass transition and the beta transition of the cement. By taking the superimposed curve to represent the long term creep behavior, a creep strain of approximately 0.6% is predicted after 400 days under a constant stress of 2 MPa.

The bone cement has been shown to undergo physical aging during storage at room temperature over 15 months. The physical aging affects both the elastic and creep behavior of the cement. The effects of aging are not included in the time–temperature extrapolation method, and consequently it is best viewed as giving a first approximation to long term creep behavior.

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