JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **12** (2001) 707–717

Effects of environment on the creep properties of a poly(ethylmethacrylate) based bone cement

J. C. ARNOLD, N. P. VENDITTI
Department of Materials Engineering, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK

The effect of test environment on the creep behavior of a poly(ethylmethacrylate) bone cement was investigated. The aim of the study was to assess the influence of environment on the inherent material behavior, and so it was convenient to perform tests in tension on well-prepared samples. In addition to control tests in air, the liquid environments studied were water, Ringer's solution and Intralipid. Creep tests were performed in each of these environments with a range of aging times, test temperatures and applied stresses. In order to compare the effects of the environments, the creep curves were fitted to a generalized form, from which a creep rate was determined. The ratio of these creep rates between different environments at each testing condition was then used as a basis for a comparison of the detailed effects of environment.

It was found that in all cases the water-based environments (water and Ringer's) had similar effects and gave the largest creep rates. Intralipid was then intermediate and air gave the lowest creep rates. These effects are mainly due to plasticization by water, although with Intralipid, some increased monomer leaching occurred, which served to reduce the creep rates. The influence of environment on the effects of aging time, temperature and stress were complex, although in general any conditions which increased water plasticization (longer aging, higher temperature and to a lesser extent, higher stress) gave an increase in creep rate. The major exception to this was at temperatures of 40 °C and above, where the effects of water plasticization were diminished, due to the inherent increase in molecular mobility of the material.

1. Introduction

PMMA bone cement has a long history of use as a medium for the fixation of prosthetic components into the body [1]. However, implant loosening, often attributed to failure of the cement is one of the major causes of implant failure [2–4]. The main reason for this is that as a relatively brittle material with a low toughness [5], PMMA is susceptible to crack formation due to static and especially dynamic loadings. This cracking can lead to cement fragmentation and eventual loosening of the implant.

The alternative bone cement studied in this investigation, based on poly(ethylmethacrylate) (PEMA) has the advantage of being a much tougher material, with a higher strain to failure of about 50%, although with a reduced modulus of about 700 MPa [6]. These compare to values of less than 10% and 2500 MPa for commercial PMMA cements. Additional advantages of the PEMA based material include a lower curing exotherm (55 °C) compared to PMMA (up to 100 °C), thus reducing the risk of bone necrosis [6, 7]. Further studies into the residual monomer content and toxicity of the cement showed the PEMA-based cement had lower monomer extractability than PMMA [8], reducing chemical necrosis, and was fully biocompatible [9, 10]. To offset these advantages, the major disadvantage of the new cement is the potential for higher levels of creep, due to a lower Tg, which can lead to dangerous amount of subsidence.

This study is the first part of an invesitgation into the creep behavior of PEMA-based cements, here focussing on the effects of test environment. Future publications will address methods for creep prediction and the effects of hydroxyapatite reinforcement, which has been shown to increase stiffness [11] and fatigue resistance [12]. It must also be recognized that in surgery the bone cement is introduced into a complex and potentially aggressive environment. It is very possible that over time these environments may adversely affect the properties of the bone cement. Changes in the interface or within the material itself could greatly contribute to implant loosening.

For many years water has been known to act as a plasticizing agent for many polymers, acting to decrease the creep resistance, but the variation in this effect at elevated temperatures, or with increased applied stress, is virtually unstudied. In fracture tests on PMMA cements performed by Hailey *et al*. [13], immersion in water led to a increase in work of fracture. With immersion in a fat-based solution, where the plasticizing effect might be expected to be greater, less of an effect was seen. The use of a fat based solution is in direct response to a need to mimic the high fat content of the bone cavity into which the cement will be implanted.

The aims of this project were to establish the general creep characteristics of the PEMA-based cement material and to study the effects on the creep properties of various storage environments at different temperatures and applied stresses. It should be emphasized that this was intended as a study of the material's inherent behavior, rather than a simulation of likely service conditions. For this reason, samples were prepared using methods that would not be practicable in an operating theater but nevertheless gave reproducible material. In addition, samples were tested in tension rather than compression and shear, and temperatures ranging from 24 °C to 50 °C were used.

The other variable that was controled was the degree of physical aging. This is a process that occurs in all glassy materials whereby there is a gradual trend towards equilibrium, resulting in increases in density, stiffness and creep resistance [14].

2. Materials and methods

2.1. Material preparation

The constituent elements of the PEMA-based cement were a powder component containing PEMA and 0.6% 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. 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 [15]. The resulting dough was then hand pressed into a 200×200 mm sheet containing twelve $70 \times 40 \times 3$ mm test piece molds. This sheet was then placed under a 750 MPa compressive stress for 30 min and the resulting specimens stored in their appropriate environments (at the testing temperature) prior to testing.

2.2. Storage environments

Four different storage and testing environments were used, as follows:

(i) air as a control;
(ii) Intralipid (Pharmacia, Milton Keynes, UK), a fat solution designed to simulate the fat in the bone cavity;
(iii) Ringer's solution (Fisons, UK), to simulate physiological salts, and
(iv) distilled water.

2.3. Weight gain measurements

The amount of water absorbed by the bone cement was measured by immersing samples in distilled water at 24 °C and at 40 °C and periodically measuring the weight an a balance accurate to 0.1 mg. Immersion was continued until a constant weight was achieved. Control samples in air were also measured at these temperatures.

2.4. Creep tests

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. This was then used to produce values of creep compliance (creep strain/applied stress). Tests were continued until either the testing time became equal to the aging time, or the sample extension reached the maximum measurable on these machines.

The effects on the creep behavior due to variations in aging time, temperature and applied stress were separately examined for each of the environments.

2.4.1. Aging

In all four environments, tests were performed on samples allowed to age in their appropriate environment at 24 °C, for 7, 14, 21 or 28 days prior to testing with a 3 MPa applied stress.

2.4.2. Temperature

To assess the effects of temperature, samples were cured and aged for 3 days at temperatures of 24 °C, 30 °C, 40 °C or 50 °C in the four environments before being testing with a 1 MPa applied stress. The lower stress level was used in this case as a 3 MPa stress produced very rapid creep rates at the higher temperatures.

2.4.3. Applied stress

Finally, 7 day aged samples were tested at room temperature with applied stresses of 1, 2, 3, 5 and 8 MPa.

In tests at room temperature, at least 5 samples were stored in 500 ml of liquid prior to testing and during testing each sample was held in an individual 500 ml environmental chamber, incorporated into the creep machine. In the cases of the temperature tests, after manufacture the specimens were placed directly in the 500 ml environmental chambers at the testing temperature. All creep testing was terminated at a time equal to the aging time, therefore, it could be said that the aging time was effectively constant and did not change significantly during the test.

The resulting creep data (compliance versus time) were fitted to Struik's universal creep equation (Equation (1)):

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

where $D(t)$ is the creep compliance, t is time, D_0 is the initial compliance, τ is a constant value equal to the inverse of the creep rate, and m is a constant.

Initially, all curves were fitted to Equation (1) to find values of all three constants. However, for simplicity it was assumed that m will be constant for all tests and D_0 will only vary with temperature. Therefore, all the creep curves were refitted using these constants in order to generate a final value of τ which was then used to compare the creep rates of each sample.

3. Results

The results of water uptake are shown in Fig. 1. From this it can be seen that the weight gain reaches a steady-state value after about 7 days at both 24 °C and 40 °C, with weight increases of 0.3% and 0.5%, respectively. It is interesting to note that the weight of samples stored in air decreases, showing that monomer is being lost. It can be assumed that monomer will also be lost from the samples stored in water, and tests involving subsequent drying of these samples showed that this is indeed the case. At 40 °C, the monomer loss rate was slightly higher in water than in air. It was hard to gain conclusive results at room temperature, as it was not possible to achieve complete drying of the samples. Nevertheless Fig. 1 shows that the samples immersed in water had a water content approaching 1% at equilibrium.

Fig. 2 shows a comparison of creep behavior between the four environments. In this case, results are shown for 14 day aged samples tested at room temperature at a stress of 3 MPa. The samples tested in air display the highest creep resistance followed by those in Intralipid with Ringer's solution and water giving the worst creep performance. The effects of a variation of aging time for samples tested in air is shown in Fig. 3. This shows that the creep resistance increases as the aging time increases, in agreement with other work on physical aging. The effects of temperature are quite dramatic, as shown in Fig. 4 for tests in air, with a large increase in creep compliance between 30 °C and 50 °C. The effects of applied stress are shown in Fig. 5 and show that the compliance increases as the stress is raised, especially above 2 MPa. As the curves are plotted in terms of creep compliance, which should account for changes in stress, it is clear that above 2 MPa, the behavior is significantly non-linear.

The curve fitting of all compliance data was very accurate with an m value of 0.244 in all but the high stress (5 and 8 MPa) tests where the value could exceed 0.5. In these cases the data was fitted to an appropriate value of m. The final values of τ for every test are displayed in Table I. As τ is inversely proportional to creep rate, similar trends to those seen in Figs 3–5 (with aging time, temperature and stress) can be seen in the τ values for the liquid environments. These are shown graphically in Figs 6–8 where the creep rates ($1/\tau$) are plotted against aging time, temperature and stress, respectively.

In an attempt to further study the effects of each environment individually, a comparison of all the creep rate values was undertaken. For example, if the 7 day aging time test performed in water were to be compared to that tested in air the creep rate values given from the curve fitting would be divided thus:

$$\frac{1/\tau_{\text{water}}}{1/\tau_{\text{air}}} = \frac{\tau_{\text{air}}}{\tau_{\text{water}}} \qquad (2)$$

This value gives an indication of how much faster the sample creeps, i.e. if $\tau_{\text{air}}/\tau_{\text{water}} = 4$, the sample tested in water has a creep rate four times that of air. All creep rates and τ value values for all environments tested under the various aging, temperature and applies stress

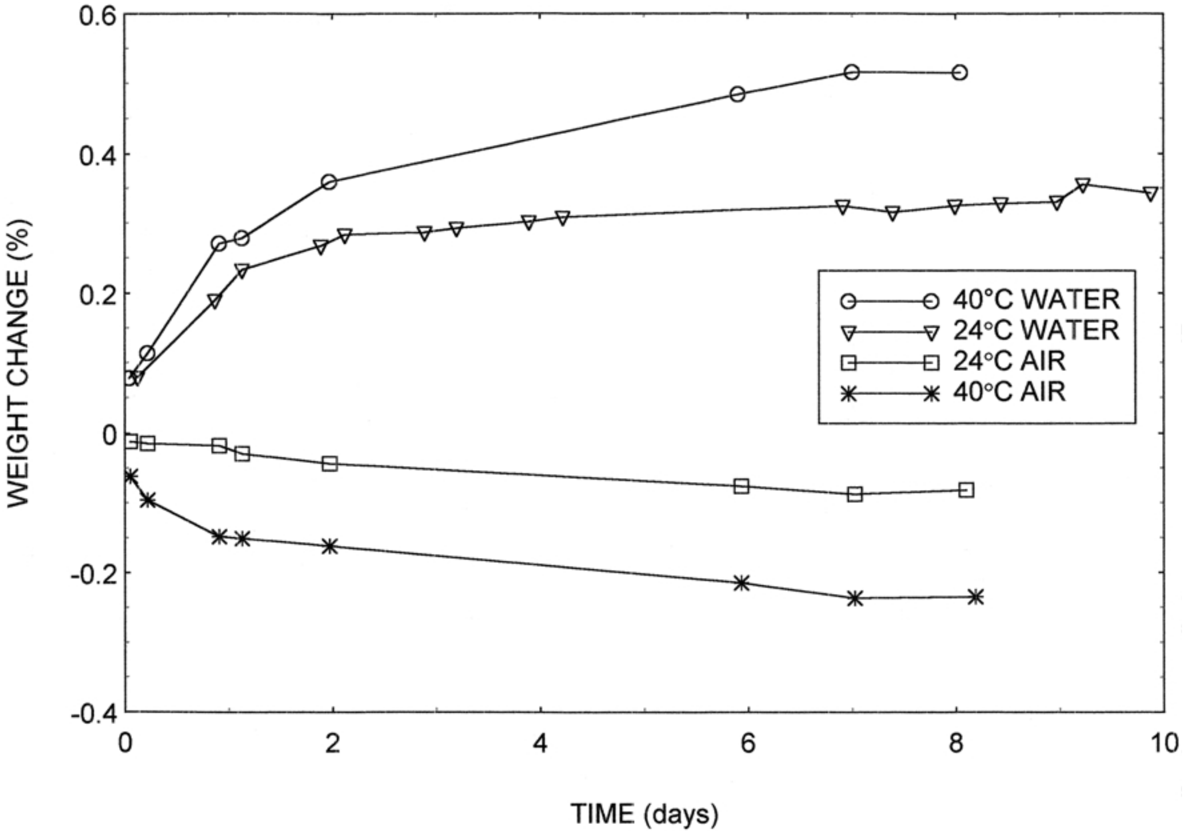

Figure 1 The weight change of samples immersed in water or left in air at 24 °C and 40 °C immediately after sample production.

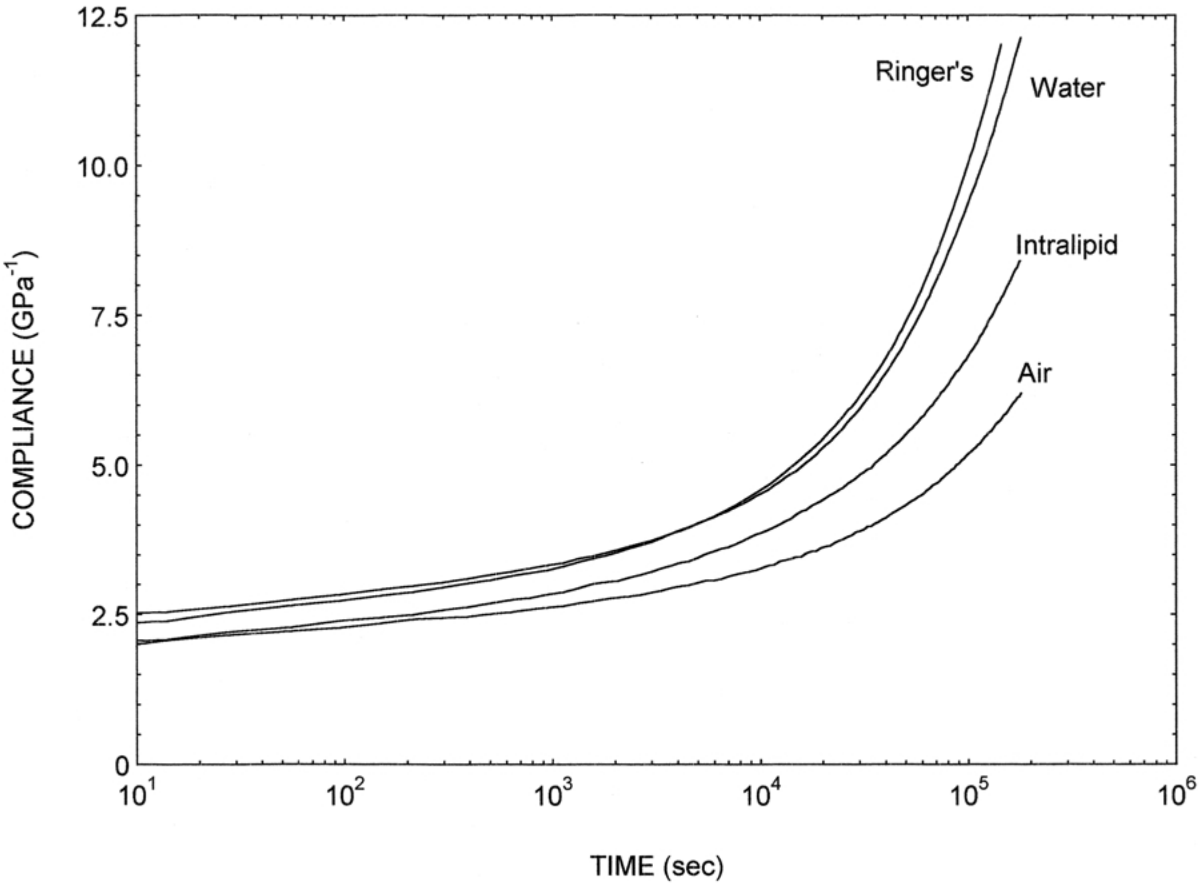

Figure 2 Variation of creep compliance with time for 7 day aged samples tested in various environments at 24 °C with an applied stress of 3 MPa.

conditions are displayed in Table II. Figs 9–11 chart the variation of these normalized τ ratios, which will be discussed more fully below.

4. Discussion

Fig. 2 shows the effects of different liquid environments compared to air at room temperature. Here it can be seen

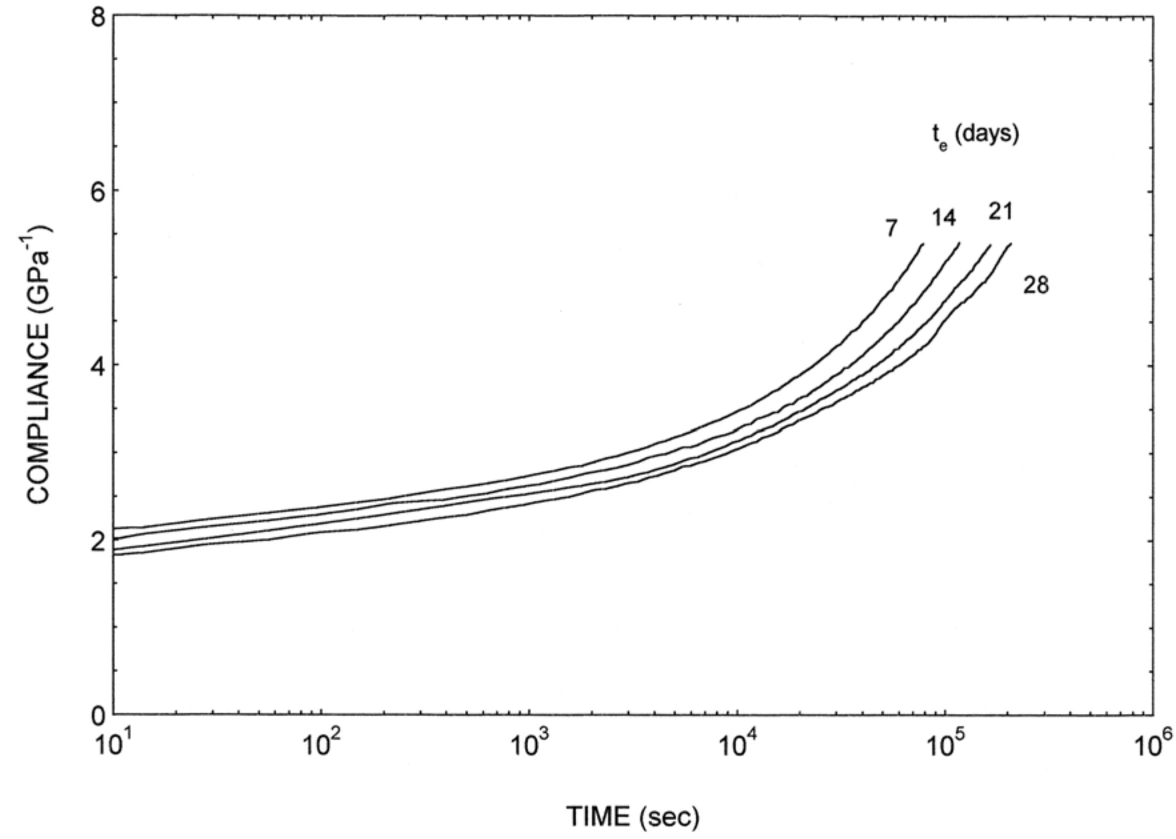

Figure 3 Variation of creep compliance with time for samples tested in air at 24 °C with an applied stress of 3 MPa after various aging times.

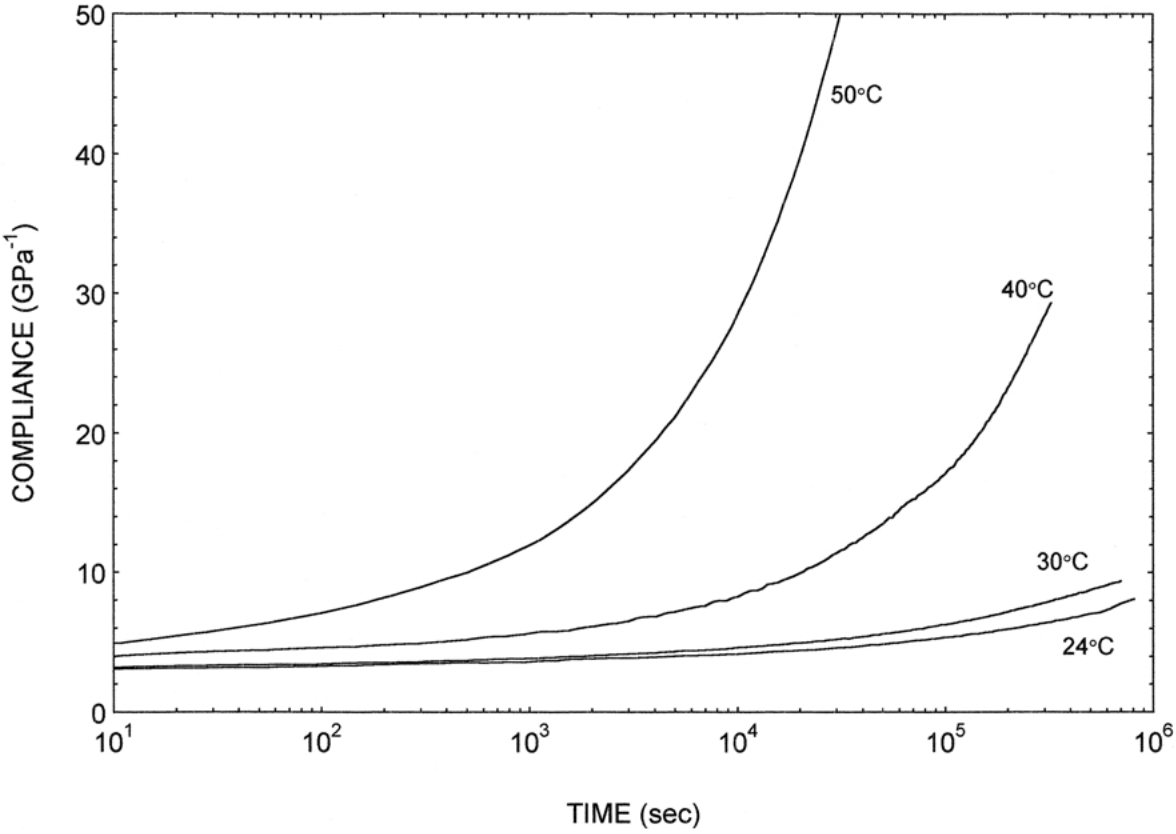

Figure 4 Variation of creep compliance with time for 3 day aged samples tested at various temperatures in air with an applied stress of 3 MPa.

that in general, Ringer's solution and water increase the creep rate to about the same degree, with Intralipid lying between these and air. Water is known to have a plasticizing effect [16–18] with the water molecules acting to break the intermolecular bonds of the polymer, therefore increasing chain mobility and reducing mechanical properties. In this respect immersion in water is comparable to a rise in temperature. The lack of variation between immersion in water and Ringer's solution implies that the physiological salts present in

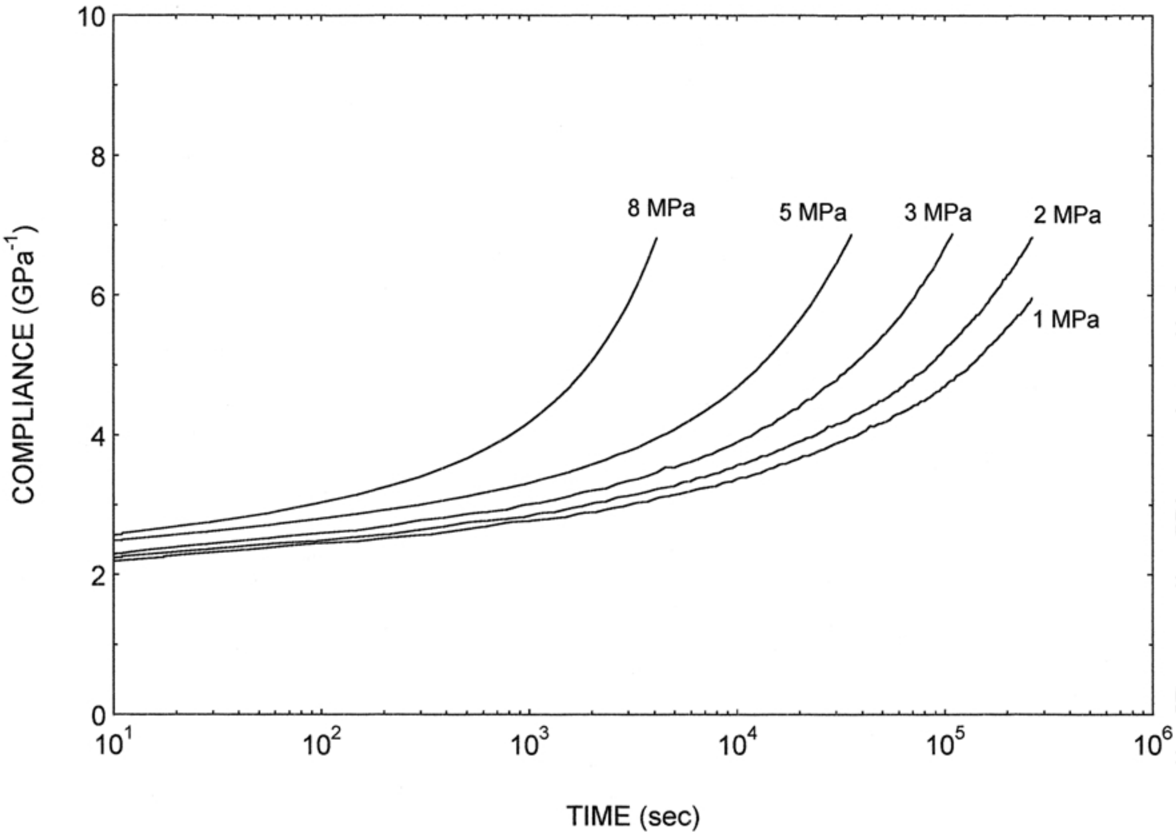

Figure 5 Variation of creep compliance with time for 7 day aged samples tested in air at 24 °C with various applied stresses.

TABLE I τ values (× 10^3 s) from Equation (1) fitted to recorded creep data for each environment under each testing condition

Aging time	Temperature	Stress	Air	Intralipid	Ringer's	Water
7 days	(24 °C)	(3 MPa)	80.8	30.3	20.7	19.3
14 days			119	54.6	28.7	26.7
21 days			183	129	33.9	31.4
28 days			226	108	48.5	47.8
(3 days)	24 °C	(1 MPa)	508	253	81.9	111
	30 °C		196	67.2	12.9	11.5
	40 °C		4.36	2.40	1.26	1.24
	50 °C		0.768	0.519	0.316	0.426
(7 days)	(24 °C)	1 MPa	137	112	54.9	48.9
		2 MPa	108	92.3	50.6	33.6
		3 MPa	80.8	30.3	20.7	19.3
		5 MPa	43.4	16.1	9.77	10.3
		8 MPa	6.08	2.80	1.20	1.88

Ringer's solution have no additional effect on the curing or creep properties. It is somewhat surprising that a relatively small amount of water (less than 1%) can have such a significant effect on the creep behavior. It is known that in glassy polymers, water tends to cluster in regions of high free volume. However, as it is also known that these regions contribute most strongly to the creep deformation, the observed behavior is not too surprising.

The increase in creep rate due to immersion in Intralipid is much smaller than that of water or Ringer's solution. In a study of the work of fracture values of PMMA bone cement in the same environments, Hailey *et al*. [19] found very similar results and concluded that the lipid emulsion has the effect of increasing the unreacted monomer release rate and therefore further curing the samples. It is very likely that a similar monomer–lipid reaction is occurring here, and the increased curing can be seen as reducing the creep rate compared to immersion in water. Further studies performed by Hailey *et al*. [13] tested commercial PMMA cement samples that had been heated to 115 °C for 15 h. This heat treatment increases the chain mobility sufficiently for continued curing to occur at a greatly accelerated rate. Tests of these samples showed Ringer's solution, water and Intralipid to have a similar effect, implying that in this case, once the monomer–lipid interreaction has been removed, Intralipid's only effect is due to the water present in the emulsion.

4.1. Influence of environment on physical aging

Fig. 9 shows the multiplication factors comparing the τ values of samples tested at the various aging times in each media. The most obvious result is that the creep rate values for Ringer's and water at all aging times are approximately equal, thus giving a τ-ratio value of one. Therefore, a comparison of Ringer's or water with other

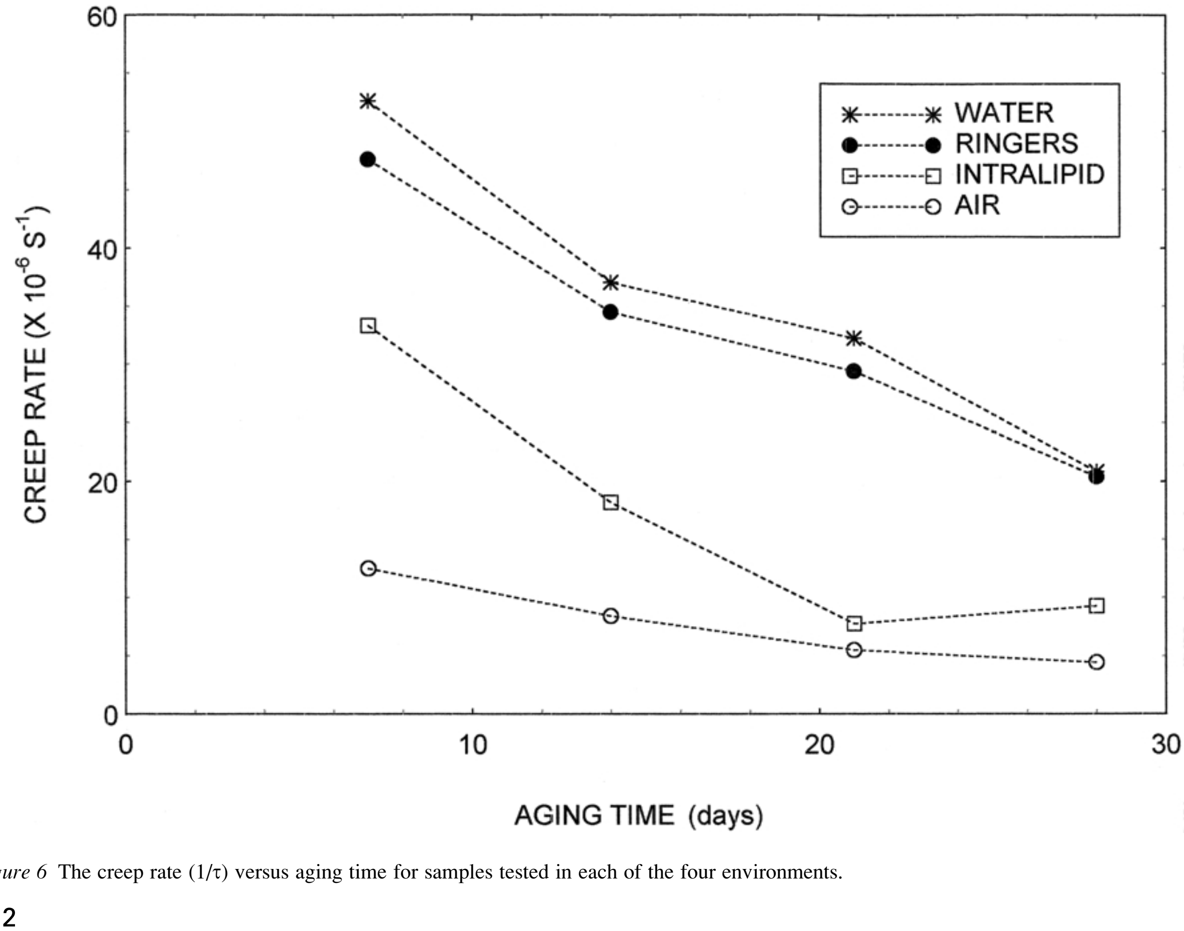

Figure 6 The creep rate (1/τ) versus aging time for samples tested in each of the four environments.

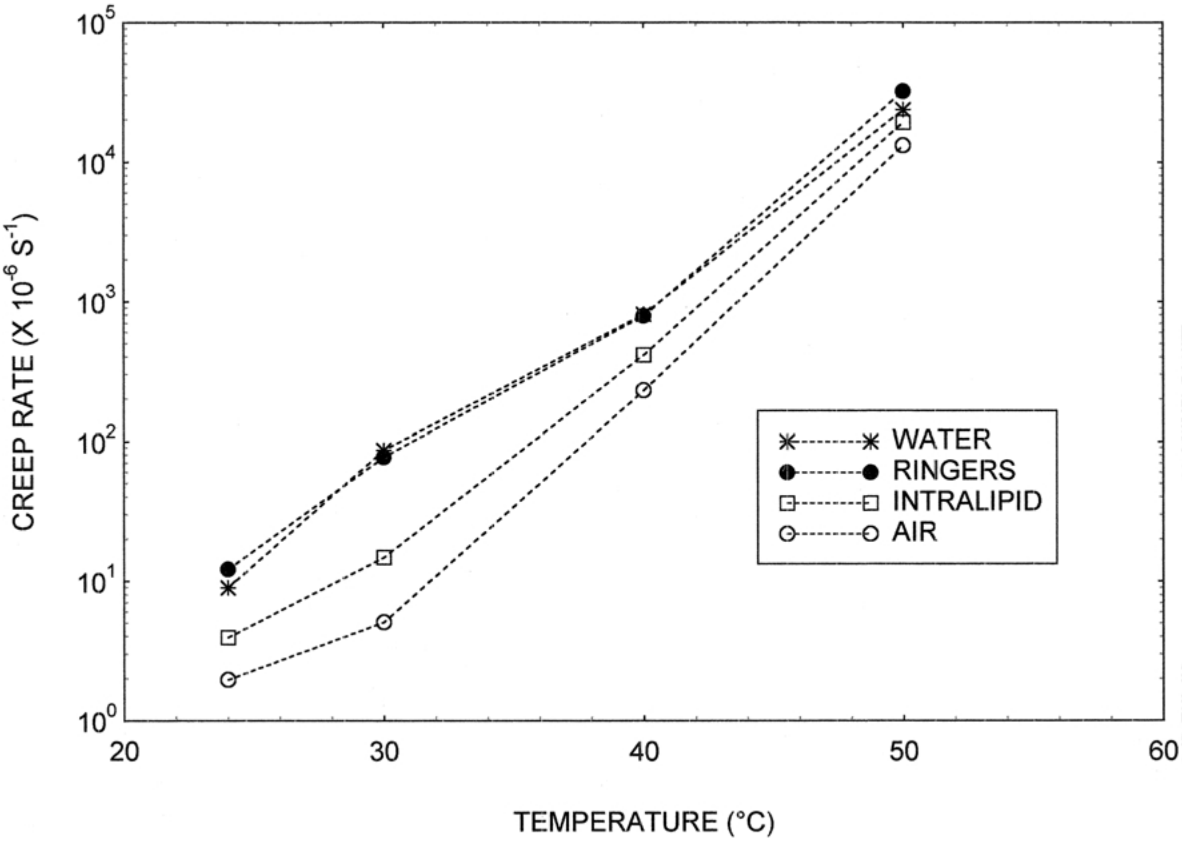

Figure 7 The creep rate (1/τ) versus temperature for samples tested in each of the four environments.

environments give very similar results. Compared to air both Ringer's and water show a general increase in ratio with aging times, with a maximum at 21 days. A similar trend is seen when Ringer's and water are compared with Intralipid, although the magnitude of the ratio value is half that when compared to air. This general increase in the τ value ratio can be considered to be a manifestation of the plasticizing effect of water. As the immersion time

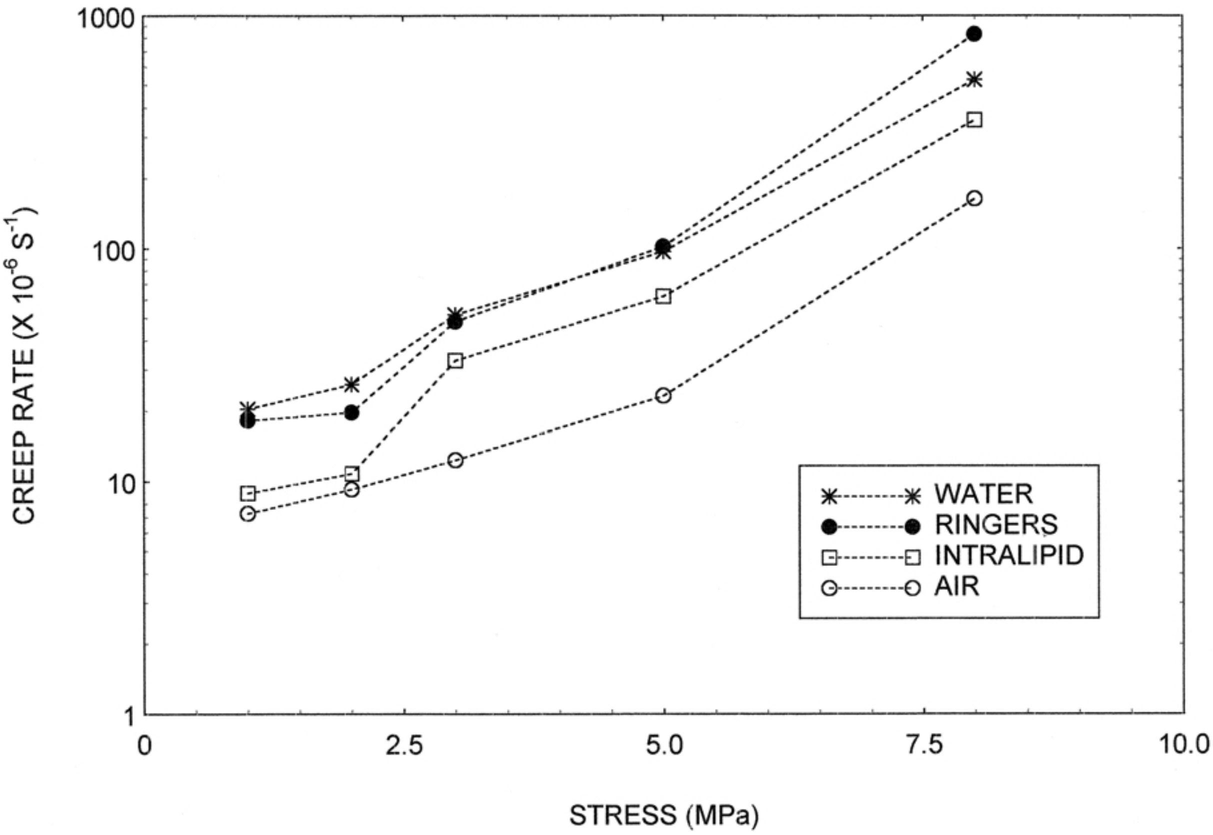

Figure 8 The creep rate (1/τ) versus applied stress for samples tested in each of the four environments.

TABLE II Comparison of the τ ratio values as described in Equation (2)

	Air/Intralipid	Air/Ringer's	Air/Water	Intralipid/Ringer's	Intralipid/Water	Ringer's/Water
7 days	2.66	4.19	3.90	1.46	1.57	1.08
14 days	2.18	4.47	4.16	1.90	2.05	1.08
21 days	1.68	5.83	5.39	3.20	3.46	1.08
28 days	1.75	4.73	4.67	2.67	2.71	1.01
24 °C	2.01	4.57	6.20	3.09	2.28	0.74
30 °C	2.92	17.10	15.21	5.21	5.86	1.12
40 °C	1.81	3.51	3.47	1.91	1.94	1.01
50 °C	1.48	1.80	2.43	1.64	1.22	0.74
1 MPa	1.23	2.50	2.80	2.04	2.29	1.12
2 MPa	1.17	2.14	3.22	1.82	2.74	1.50
3 MPa	2.66	3.90	4.19	1.46	1.57	1.08
5 MPa	2.70	4.45	4.20	1.65	1.56	0.94
8 MPa	2.17	3.24	5.07	2.33	1.49	0.64

increases, the samples are further plasticized, increasing the free volume and chain mobility of the material and the creep resistance is decreased leading to a larger difference in the creep rates compared to values measured to air. The greatest difference is seen in the 21 day aged samples and this could be an indication of a benchmark in the uptake of water and plasticization of the polymer. Therefore at this point the plasticization effects of the water-based environments reach a maximum and the differences between the water based environments and air are the greatest.

When Intralipid is compared with air the trend is reversed and the τ ratio decreases with increasing aging time, with a minimum at 21 days. The effects of Intralipid on the cement can be considered to be a balance of the plasticizing effect of the water present, increasing the creep rate, and the increased monomer leaching, acting to increase the cement's creep resistance. Samples tested after 7 days aging in Intralipid have creep rates less than the samples immersed in water and Ringer's, but higher than those tested in air. This result would imply that the plasticizing effects of water uptake has the upper hand, but the accelerated curing caused by the monomer leaching is strengthening the creep resistance. After 14 days aging, the effects are similar but the increased rate of curing is taking a larger proportion of the overall effect, and the τ ratio value shown in Fig. 9 has decreased. After 21 days the τ ratio value compared to air is at a minimum. From the results of samples immersed in Ringer's and water it is possible to say that 21 days marks the saturation point of water, and therefore the plasticization effect will be at its greatest. However, as the plasticization due to water will increase free volume it will also allow greater diffusion of lipid into the material, increasing monomer loss. This effect will, therefore, also reach a maximum at about 21

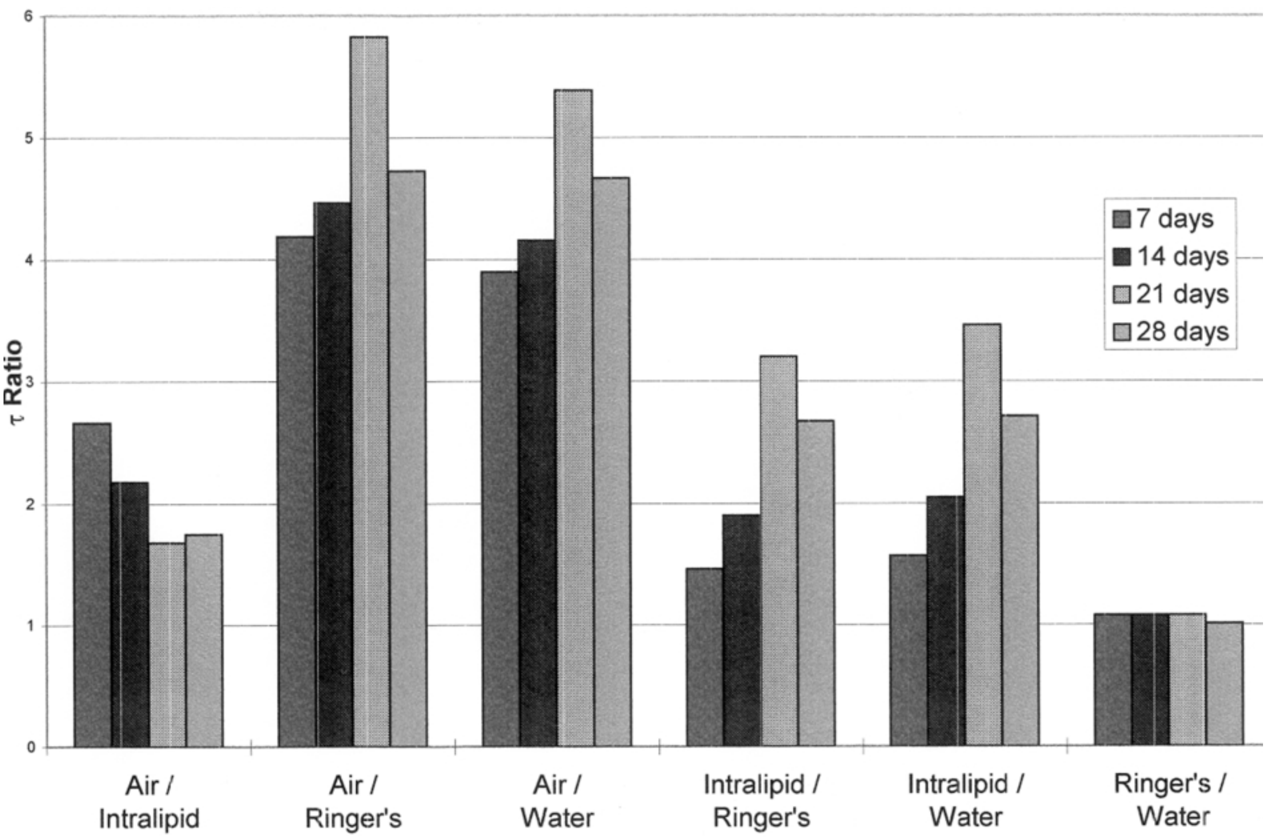

Figure 9 Comparison of the ''normalized'' τ ratio values for all aging tests performed in the four environments.

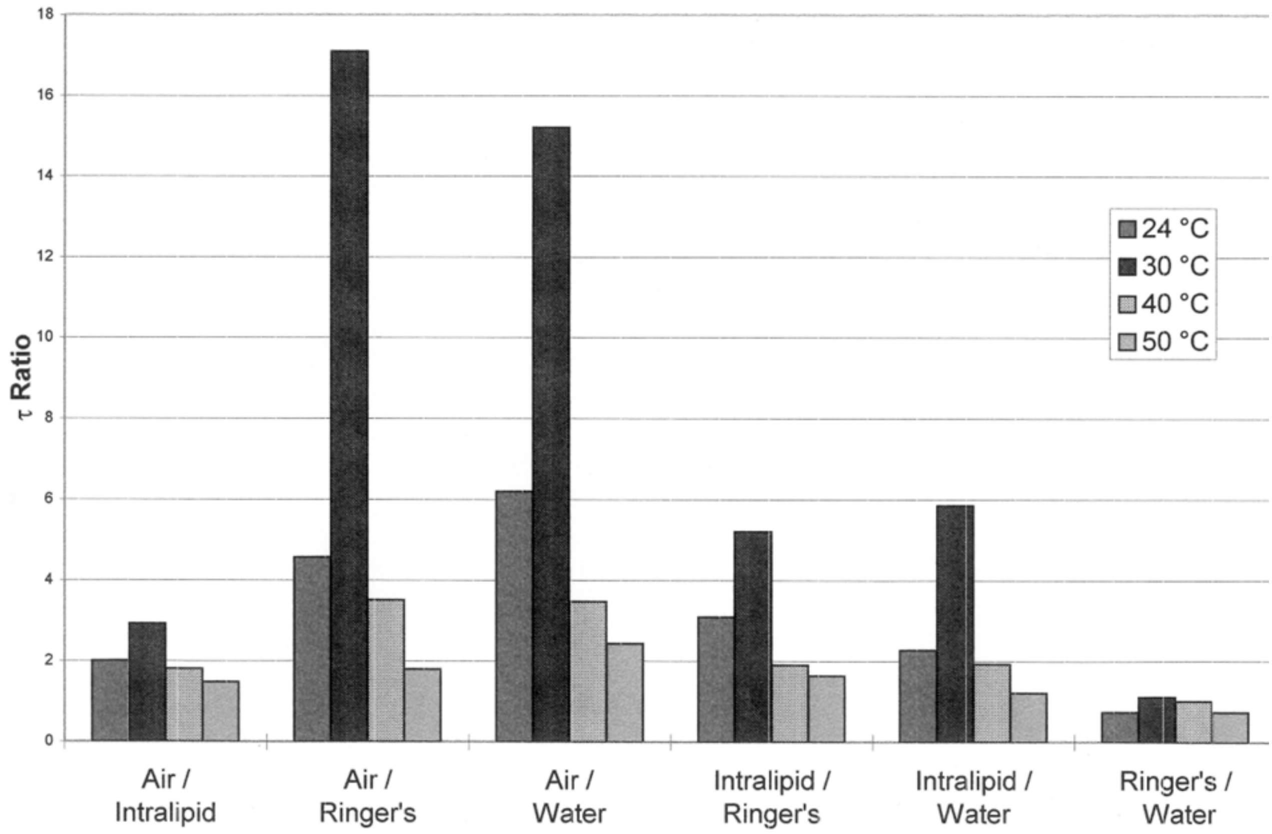

Figure 10 Comparison of the ''normalized'' τ ratio values for all temperature tests performed in the four environments.

days. At longer aging times, the ratio compared to air increases, suggesting that water plasticization is becoming more significant, presumably because the monomer loss has now effectively stopped.

4.2. Influence of environment on temperature effects

Fig. 3 shows the typical response to an increase in temperature, with a very dramatic increase in creep rate.

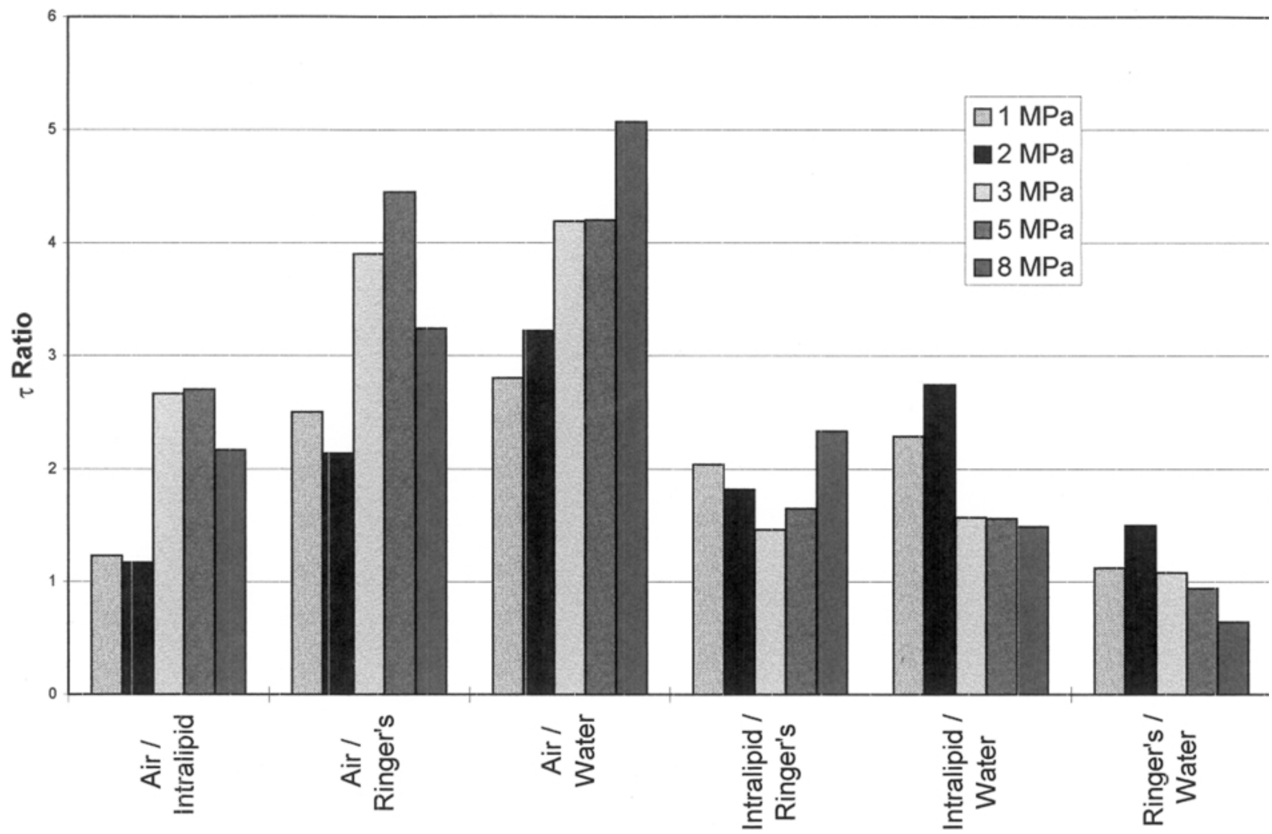

Figure 11 Comparison of the ''normalized'' τ ratio values for all stress tests performed in the four environments.

The comparison of the environment on the effects of temperature can be seen in Fig. 7, where the creep rates are plotted and in Table II and Fig. 10, where the τ ratios are displayed. Similarly to the results of the aging tests, the samples immersed in water and Ringer's show very few differences and therefore the comparisons with water or Ringer's with the other environments will be practically identical. Comparing Ringer's or water with air, there is a general downward trend in τ ratio values with increasing temperature, but with a dramatic increase at 30 °C. A downward trend towards a value of one indicates that as temperature increases the creep rates of Ringer's and water samples move ever closer to those of samples in air. It must also be noted that a similar trend is seen comparing Intralipid with air however, with a far less dramatic jump at 30 °C.

At room temperature the results are very similar to the 7 day aging test. However, at 30 °C the τ ratio values compared to air increase dramatically. Obviously as temperature increases, the mechanical properties will decrease but this only explains the increase in creep rate seen in all environments, including air. A likely explanation for this dramatic jump in τ values is given below.

An increase in temperature will increase the free volume of the system, leading to a greater uptake of liquid, as indeed can be seen in Fig. 1, which will increase the effects of plasticization. This increase in water uptake and the subsequent decrease in the creep resistance of the samples immersed in water-based environments can be used to explain the enormous differences between samples immersed in water and Ringer's, at 30 °C, and those in air. The same effect, although to a much reduced extent, is seen when comparing Intralipid and air. Here the lipid–monomer reaction also gets an increase in internal energy and reduces the creep rate sufficiently to suppress the effects of water uptake seen in water and Ringer's samples.

At 40 °C the general effects of increased temperature start to overtake the effects of increased water uptake and the creep rates of samples tested in liquid environments begin to move closer to those tested in air until at 50 °C.

In all tests performed at 50 °C the τ ratio is significantly reduced, with the highest τ ratio only being 2.4 and therefore, it can be said that the effect of the environment is diminished. This is probably due to the fact that at this higher temperature, the chain mobility of the material has increased to such an extent that any additional plasticization by water has little effect.

4.3. Influence on stress effects

Fig. 5 shows the typical response of an increase in stress on the creep compliance, from which it can be seen that above 2 MPa, the compliance increases quite markedly with increasing stress. This shows that the material behaves non-linearly above 2 MPa. Fig. 8 shows how the creep rates vary with stress for each of the environments and Fig. 11 charts the τ ratio values. Again the similarity of immersion in Ringer's and water is clear as the comparisons display an average value of one. In this case, however, there is a slight trend for higher creep rates in Ringer's at higher stresses. This could possibly be due to the increased stress overcoming osmotic forces in the Ringer's solution to give an increase in plasticization, but the effect is small and inconclusive.

With the other comparisons, the changes in τ ratio values are smaller than seen with aging time and temperature, and so sample to sample variability causes some scatter. The main trend that is observable is that for all the liquid environments, the *t*-ratio compared to air increases as the stress increases. A probable explanation for this is that at higher stresses, the initial loading will increase the free volume by a greater amount than at low stresses, even to the scale of increasing pore sizes. The consequence of which will be a greater amount of water intake and therefore, a further increase in creep rate due to the increase in plasticization.

The Intralipid seems to undergo a dramatic increase in creep rate (and hence t ratio compared to air) between 2 and 3 MPa. Again, this is almost certainly due to an increase in plasticization from water uptake, but indicates that in this case, there is a threshold stress, above which water uptake is dramatically increased. This may again involve the overcoming of osmotic forces, and it is interesting that it occurs at the same stress level at which the material departs from linearity.

5. Conclusions

This study has shown that the testing environment has a dramatic effect on the creep behavior of the PEMA-based bone cement. The basic variation is that as the water content of the environment increases, the creep rate increases, due to water uptake and plasticization. Storage of specimens in water or Ringer's solution has the effect of increasing the creep rate by between 2.5 and 6 times at room temperature for all aging times and applied stresses tested. An additional effect occurs with Intralipid, where the effects of unreacted monomer leaching are important for at least 2 weeks after sample preparation. These effects are relatively well known, however, the effects of environment on the variation of creep rate with aging, temperature and stress are comparatively unstudied.

The study has shown that the physiological salts present in Ringer's solution have no significant effect on the creep properties of this cement, and can be therefore assumed to have no effects on the chemical composition of the material. The only exception to this is a slight effect on the variation of creep rate with stress, possibly due to osmotic forces.

At elevated temperatures, the effects of different environments change. At the highest temperature studied, all tests yielded very similar creep rate results, as the molecular mobility of the material had increased to the extent that additional water plasticization has little effect. At an intermediate temperature of 30 °C, however, the plasticizing effect of an increased uptake of water produces the highest ratio of all tests. This effect has virtually gone at 40 °C, and so between these temperatures, the effect of environment will change dramatically with a small change in temperature. This has obvious significance for testing at body temperature.

The effects of aging are of slightly less significance, with additional water uptake increasing creep rates for aging times of up to 3 weeks, except for Intralipid, where monomer leaching dominated. The effects of increased stress are least dependent on environment, but are again dominated by water uptake, with an increased stress allowing greater plasticization and a higher creep rate.

It is obvious that the testing environment has an enormous effect on the properties of this bone cement and it is, therefore, extremely important that factors such as temperature, stress and, just as importantly, aging time, are given consideration. To replicate *in vivo* conditions it could be argued that a fat-based solution should be used for testing, however, the use of water or Ringer's solution maybe useful to act as a worst case scenario.

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Received 4 February
and accepted 14 August 2000