

Analysis of rheological properties of bone cements

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Abstract The rheological properties of three commercially available bone cements, CMW 1, Palacos R and Cemex ISOPLASTIC, were investigated. Testing was undertaken at both 25 and 37 °C using an oscillating parallel plate rheometer. Results showed that the three high viscosity cements exhibited distinct differences in curing rate, with CMW 1 curing in 8.7 min, Palacos R and Cemex ISOPLASTIC in 13 min at 25 °C. Furthermore it was found that these curing rates were strongly temperature dependent, with curing rates being halved at 37 °C. By monitoring the change of viscosity with time over the entire curing process, the results showed that these cements had differing viscosity profiles and hence exhibit very different handling characteristics. However, all the cements reached the same maximum viscosity of 75×10^3 Pa s. Also, the change in elastic/viscous moduli and $\tan \delta$ with time, show the cements changing from a viscous material to an elastic solid with a clear peak in the viscous modulus during the latter stages of curing. These results give valuable information about the changes in rheological properties for each commercial bone cement, especially during the final curing process.

Introduction

Acrylic bone cement is widely used in orthopaedic surgery for total joint replacements as a means of fixation of the prosthesis to the bone. It functions by stabilizing the prosthesis, filling the gap between the prosthesis and the surrounding bone, and transmitting load from the prosthesis to the bone [1, 2].

Bone cement is a self-curing polymer, consisting of a powder polymer, containing mainly polymethylmethacrylate (PMMA) or PMMA-styrene co-polymer beads, and benzoyl peroxide; and a liquid monomer, methylmethacrylate. On mixing the powder and liquid together, polymerization occurs by a free radical reaction [2, 3], changing the cement from a viscous liquid to a hard, elastic solid. This process takes approximately 10–15 min, allowing the surgeon only a few minutes of working time to mix the cement and either inject it with a cement gun, or manually place into the body. Once in the body, the cement must still be liquid enough to be able to penetrate into the interstices of trabecular bone [2].

Understanding the flow characteristics or rheology of bone cement is important because upon mixing the liquid monomer and powder polymer together, the handling properties of the cement exhibit three different phases. These phases are known as dough time, setting time and working/handling time. Dough time is the time from when all of the liquid is added to the powder, to the time at which the cement mass no longer adheres to a surgically gloved finger [3]. Setting time is the elapsed time from start of the mix to the temperature midway between peak curing temperature and ambient temperature [4]. Handling/working time is the difference between dough time and setting time.

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Handling time includes both the period when the material is readily workable and the subsequent period when it is hardening [3].

Very little work has been undertaken on the rheological properties of bone cement, unlike the extensive work and literature produced on their static and dynamic mechanical properties [5–10]. Previous work on the rheological properties have included creep [11–13], stress relaxation [12, 14], temperature profiles of cements during curing [15], and cements characterized by rotational [16, 17] and capillary extrusion rheometers [17]. A comprehensive and extensive study was produced by Farrar and Rose [18]. They used a parallel plate rheometer to characterize the initial rheological properties (i.e. during the dough phase) of a variety of low and high viscosity cements, including Palacos R, at a variety of temperatures (19, 21, 23 and 25 °C). Using the rheometer, measurements were made of viscosity, storage modulus, loss modulus and phase angle, δ , against time until the viscosity of the cement tested reached between 1,000 and 1,500 Pa s. Their results showed that the time taken to reach the desired viscosity decreased with increasing temperature as expected, and showed an Arrhenius dependence. Furthermore they showed that the increase in viscosity with time varied with each type of cement. Much of their work involved explaining the factors involved in the initial rise in viscosity such as phase volume of PMMA particles and swelling of the polymer beads. A more recent study was undertaken by Hernandez et al. [19]. They produced similar work to Farrar and Rose, by studying the rheological properties of a variety of experimental bone cements during the dough and handling phases at 25 °C. Their results also showed that the increase in viscosity with time varied with each formulation of cement.

The object of the work in this study was to examine the rheological behaviour of a variety of high viscosity bone cements during the entire curing process, therefore covering a wider range of viscosities, up to 80×10^3 Pa s, with respect to the work published by Farrar and Rose. This rheological behaviour was studied both at room temperature (25 °C) and body temperature (37 °C), the latter not having been investigated before.

Theoretical considerations

Viscoelasticity

Bone cement, like most polymers is a viscoelastic material and so has viscous and elastic components [20]. These materials change their properties with

temperature and time. One way to look at these changes is by measuring the response of the material to deformation by periodic forces, e.g. during forced vibration or small-amplitude oscillatory shear. The response obtained shows that stress and strain are not in phase, the strain lags behind the stress by a phase angle, δ , known as the loss angle [20–22].

If the oscillatory shear is sinusoidal, then

$$\tau = \tau_o \sin \omega t \quad (1)$$

where τ = shear stress; τ_o = stress amplitude; ω = angular frequency; t = time;

and

$$\gamma = \gamma_o \sin(\omega t - \delta) \quad (2)$$

where γ = shear strain; γ_o = strain amplitude.

The equation for stress Eq. (1) can be expanded to give

$$\tau = \tau_o \sin \omega t \cos \delta + \tau_o \cos \omega t \sin \delta \quad (3)$$

This shows that the stress can be resolved into two components: $\tau_o \cos \delta$ which is in phase with the strain and $\tau_o \sin \delta$ which is $\pi/2$ out of phase with the strain. Therefore, two dynamic shear moduli (G) can be defined: G' which is in phase with the strain and G'' , which is $\pi/2$ out of phase with the strain. As $G' = (\tau_o/\gamma_o) \cos \delta$ and $G'' = (\tau_o/\gamma_o) \sin \delta$, Eq. (3) becomes

$$\tau = \gamma_o G' \sin \omega t + \gamma_o G'' \cos \omega t \quad (4)$$

This leads to the phase angle δ being

$$\tan \delta = G''/G' \quad (5)$$

Complex notation is often used and so the stress and strain become

$$\tau = \tau_o \exp i(\omega t + \delta), \quad (6)$$

and

$$\gamma = \gamma_o \exp i\omega t \quad (7)$$

where $i = \sqrt{-1}$

The overall complex modulus $G^* = \tau/\gamma$ is then given by

$$G^* = \frac{\tau_o}{\gamma_o} \exp i\delta = \frac{\tau_o}{\gamma_o} (\cos \delta + i \sin \delta) \quad (8)$$

Therefore by using the earlier definitions of G' and G''

$$G^* = G' + iG'' \quad (9)$$

G' and G'' are called the real and imaginary components of the modulus, respectively. They are also known as the storage and loss moduli.

Measurement of dynamic viscoelastic properties

Different methods can be used to measure the dynamic viscoelastic behaviour of materials such as oscillatory strain, wave propagation and steady flow [21]. The oscillatory methods involve either free or forced oscillations either in tension or shear.

A controlled shear stress rheometer applies a torque (forced oscillation) and measures the resultant displacement. The sample is subjected to a periodic deformation and its periodic response and phase lag (δ) are measured and recorded. From this, the phase angle, complex, elastic and viscous moduli, complex viscosity as well as shear stress and strain, are calculated.

The test material can be contained either between two parallel plates, or a cone and plate, the angle between the cone and plate being less than 4° [21]. There are advantages and disadvantages with each of these methods. The parallel plate system consists of a fixed bottom plate and a rotating upper plate and the sample is placed in between. The gap between the plates can easily be set to a fixed amount. However, the shear rate produced is not constant across the sample—it varies from zero at the centre to a maximum at the edge, and so the software takes an average of this shear rate. One of the main advantages of this system is that it can be used with particulate materials. In the cone and plate system, the shear rate stays nearly constant across the sample, but if particulate materials are being tested the particles may ‘jam’ at the cone apex resulting in noisy data. It can also be difficult to set the correct gap/cone angle. As bone cement is a particulate material, the parallel plate system is the most appropriate to use.

Materials and methods

The bone cements tested were:

Cemex ISOPLASTIC (Tecres S.p.A. Italy).

CMW 1 (CMW, Blackpool, UK).

Palacos R (Schering-Plough Ltd, Brussels, Belgium).

A Bohlin Instruments CVOR 200 rheometer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) was

used to measure the change in rheological properties of these cements during curing, using the parallel plates measuring system. The diameter of the upper parallel plate measured 40 mm and the gap between the two plates was set at 2 mm. Approximately 4 g of each cement was mixed by hand and placed between the plates of the rheometer. The top plate was lowered and the excess cement carefully removed. The rheometer was used in continuous oscillation mode with a frequency of 5 Hz. This rheometer has isothermal temperature options allowing the temperature of the bottom plate of the measuring system to be set to a desired temperature, and so the cements were tested at both room temperature (25°C) and body temperature (37°C).

The time of 90 s elapsed from the onset of mixing each cement until the first rheometer reading. The rheometer was set to take readings every 6 s and continued until the bone cement became so solid that the top parallel plate was no longer able to oscillate at a frequency of 5 Hz.

Results

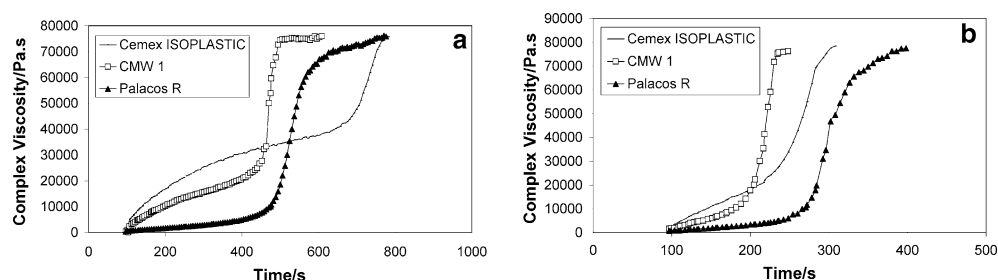
The times taken for the different bone cements to cure, signified by a constant elastic modulus, are shown in Table 1. The results show that at 25°C , CMW 1 cured at a much faster rate than Palacos R and Cemex ISOPLASTIC bone cements. Both Palacos R and Cemex ISOPLASTIC took a similar length of time to cure. At 37°C (body temperature) all the cements cured at a much faster rate than at room temperature, however, the differences in the length of time for the cements to cure were much smaller, with CMW 1 curing the fastest, followed by Cemex ISOPLASTIC, then Palacos R.

Figure 1a and b are graphs (using one representative sample at each temperature), showing how the viscosity increases with time at 25°C and 37°C , for each of the three cements. They clearly show how much faster the viscosity increases with time (i.e. cement cures) at 37°C than at 25°C , which is to be expected given that curing rates are temperature-dependent. Cemex ISOPLASTIC cures 2.5 times more rapidly at 37°C than at

Table 1 Curing/setting times of bone cements at 25°C and 37°C

Material	Cure time at 25°C / min (mean \pm SD)	Cure time at 37°C / min (mean \pm SD)
Cemex ISOPLASTIC	12.9 \pm 0.2	5.1 \pm 0.2
Palacos R	12.8 \pm 0.1	6.6 \pm 0.1
CMW 1	8.7 \pm 0.4	4.1 \pm 0.5

Fig. 1 Viscosity during setting of Cemex ISOPLASTIC, Palacos R and CMW 1: (a) at 25 °C, (b) at 37 °C



25 °C, CMW 1, 2.1 times, and Palacos R 1.9 times. For all the cements, the viscosity reached a maximum at approximately 75×10^3 Pa s. This is the point at which the cement is no longer a viscous liquid but an elastic solid. Again these graphs also show that at both temperatures CMW 1 cures much faster than either Palacos R or Cemex ISOPLASTIC. However, Palacos R and Cemex ISOPLASTIC both take similar times to cure at 25 °C, but Cemex ISOPLASTIC cures faster than Palacos R at 37 °C.

Figure 2a–f are graphs (again using one representative sample at each temperature), showing the elastic modulus, viscous modulus and $\tan \delta$ for each material at 25 and 37 °C.

Discussion

The rheological properties of bone cements during their curing phase are very important in determining their mixing/handling characteristics and viscoelastic properties. Furthermore, these properties have a significant influence on material porosity, ability to penetrate into the bone and the ultimate strength of the cement/prosthesis interface.

It is clear from the results that there are differences in the rheological properties of the three cements during their curing cycles. The most pronounced is the faster setting time of CMW 1 in comparison to Cemex ISOPLASTIC and Palacos R. In addition increasing cure temperature significantly speeds up setting time, however, has little effect on ultimate elastic modulus.

Figure 1a and b have important differences when studied in detail. They both show three different phases, (1) an initial increase in viscosity followed by (2) a plateau (where the viscosity increases slightly), and then (3) a final rapid increase in viscosity. According to Farrar and Rose [18] there are two different processes, which account for these different increases in viscosity. The first is when the PMMA beads are added to the methylmethacrylate monomer, the beads themselves absorb some of the monomer and swell. This leads to the initial increase in viscosity. The

second (final) rise in viscosity is then due to the polymerization reaction.

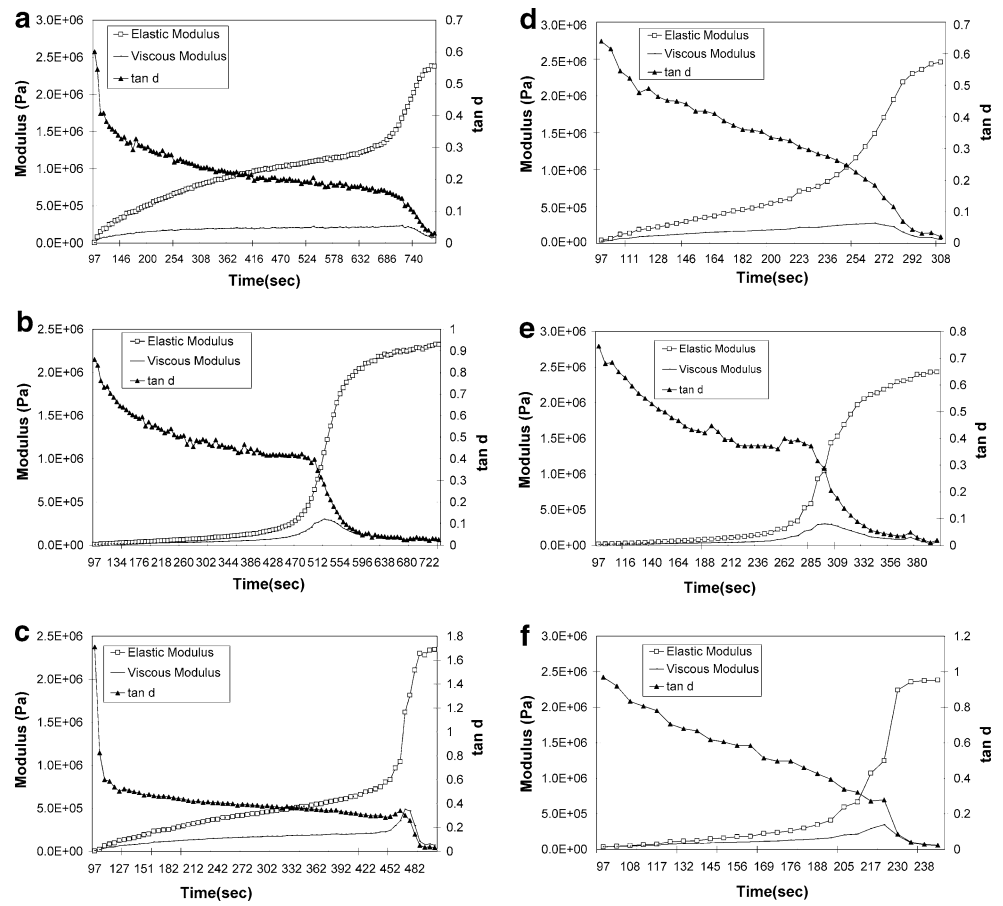
A comparison of the cements at the three different viscosity phases is given below:

1. *Initial increase.* Cemex ISOPLASTIC bone cement at both temperatures showed the largest/most rapid increase in viscosity, and its viscosity at this stage was much higher than the other two bone cements. Palacos R showed the least increase, and had the lowest viscosity of all the cements at this point. For Palacos R there appeared to be no differentiation between this stage and the plateau stage. CMW 1 lies in between the two.
2. *Plateau.* The viscosity of Cemex ISOPLASTIC is again much greater than the other two, and showed a gradual increase with time. The average viscosity was approximately 30×10^3 Pa s (at 25 °C). Palacos R had the lowest viscosity (ave. 3.0×10^3 Pa s at 25 °C), and CMW 1 again lay between the two (15×10^3 Pa s).
3. *Final increase.* In the latter stages of curing, the viscosity suddenly increased reaching a maximum (approximately 75×10^3 Pa s) when the cement finally became a solid. CMW 1 was found to cure/polymerize the fastest at this point followed by Palacos R then Cemex ISOPLASTIC.

At 25 °C, Palacos R then showed a further final plateau, unlike the other cements. This may be unique to Palacos R or may be due to the other cements becoming so stiff that the rheometer was unable to oscillate at 5 Hz (and so unable to take more readings) leading to this stage being missed. Recent work by Hernandez et al. [19] also showed differing viscosity profiles for the different formulations of experimental cements, with viscosities reaching a maximum of 80×10^4 Pa s.

At 37 °C all the graphs are similar, but have a much shorter initial and plateau region, especially Cemex ISOPLASTIC. Essentially the increase in temperature has led to the polymer beads absorbing the monomer and swelling more rapidly, and also increasing the rate of polymerization.

Fig. 2 Viscoelastic properties during setting of (a) Cemex ISOPLASTIC at 25 °C, (b) Palacos R at 25 °C, (c) CMW 1 at 25 °C, (d) Cemex ISOPLASTIC at 37 °C, (e) Palacos R at 37 °C, (f) CMW 1 at 37 °C



Examination of Figure 2a–f, (where the elastic modulus = real modulus, G' , the viscous modulus = imaginary modulus, G'' , and δ = phase/loss angle) reveals that initially both the viscous and elastic moduli increase, with the elastic modulus increasing much more rapidly as the cement changes from being a viscous liquid to an elastic solid. In the early stages of polymerization tan δ was very large due to the ratio between the viscous and elastic modulus being large, but as the cement cured, this ratio became much smaller, leading to tan δ becoming almost zero.

For all of the cements tested there was a peak in the viscous modulus. This occurs during the transition of the cement, i.e. when it changes from being a viscous liquid to an elastic solid. It is interesting to note that this peak does not always occur at the same point on all the graphs. In CMW 1 it occurred at the very end of curing as expected, with Palacos it was very near the end but the cement still appeared to carry on curing. With Cemex ISOPLASTIC there was not a sudden peak, but a gradual build up over the whole curing process. The peaks in G'' (viscous modulus) and tan δ (see figure 2a–f) occur when there is some kind of molecular motion, such as rotation of side groups, in

the polymer structure [20]. The peaks are a damping effect i.e. energy is not stored but is dissipated mainly as heat [23]. This causes an increase in free volume, which allows space for the molecules to move. Previous work on commercial cements by Farrar and Rose [18] missed these peaks in viscous modulus and tan δ , due to viscosity measurements being stopped at 1,000–1,500 Pa s. However, work produced by Hernandez et al. [19] clearly show peaks in tan δ for some of their cement formulations.

The point at which the cement has cured can clearly be seen when the elastic modulus reaches a maximum and both viscous modulus and tan δ reach a minimum. The elastic modulus increases in a very similar way to the complex viscosity, but only showing two distinct phases: a slow gradual increase followed by a final rapid increase. This final rapid increase in elastic modulus occurs during polymerization, reaching a maximum when the cement is fully cured. Only Cemex ISOPLASTIC at 25 °C shows an initial increase in elasticity followed by a plateau region before finally curing.

As CMW 1 has the shortest overall setting time, it therefore has the shortest handling time of all three cements at both 25 and 37 °C, whereas Palacos R has the

longest handling time at 37 °C, and Cemex ISOPLASTIC the longest at 25 °C. This has implications for the choice of cement, depending on the surgical procedure.

Conclusions

This study shows that the three high viscosity cements tested show distinct differences in curing rate, with CMW 1 curing in 8.7 min at 25 °C and both Cemex ISOPLASTIC and Palacos R curing in 13 min at 25 °C. It also shows that the curing time is approximately halved when the testing temperature is increased to 37 °C, with CMW 1 taking 4.1 min, Cemex ISOPLASTIC, 5.1 min and Palacos R 6.6 min.

The change in viscosity with time during the curing process was very different for each cement. During the early stages of curing Cemex ISOPLASTIC was the most viscous, and Palacos the least viscous, with CMW 1 rapidly becoming the most viscous during the latter stages of curing.

The handling times for each cement were also very different, with CMW 1 having the shortest handling time at both temperatures, and Cemex ISOPLASTIC the longest at 25 °C and Palacos R at 37 °C.

Knowing the curing rate and handling times of bone cements as well as the mechanical properties means that the surgeon can make a more informed choice of which is the most ideal bone cement to use.

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