Ultrasonic characterization of the mechanical properties and polymerization reaction of acrylic-based bone cements

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Abstract: In this investigation the pulse-echo technique was validated as a method that could be used to monitor the complete polymerization of acrylic bone cement in a surgical theatre. Currently, orthopaedic surgeons have no objective method to quantify the state of cure of bone cement as it progresses through its polymerization cycle. Clear benefits of the pulse-echo technique are that it is easy to use, non-invasive, and non-destructive. Furthermore, the test results were found to be highly reproducible with minor deviations. Three proprietary cements were used to confirm the validity of the technique; CMW® Endurance, Palacos® R and Simplex P™. The results showed that the acoustic properties of bone cement clearly demonstrated a relationship with the different stages of polymerization, and in particular with the transitions between the waiting, dough, and setting phases. Additionally, the cure time of the poly(methyl methacrylate) cements consistently correlated with the attainment of 75 per cent of the average maximum velocity of sound value. The measured cure times concurred with the ISO and ASTM standards. Moreover, measurements of the final sound velocity and broadband ultrasonic attenuation correlated strongly with the density and mechanical properties of the cured bone cement samples.

Keywords: velocity of sound; curing process; pulse-echo technique; physical properties; poly(methyl methacrylate) bone cement

1 INTRODUCTION

Acrylic bone cements play an integral role in joint arthroplasty surgery, to ensure prosthesis fixation to bone. They are two component systems composed mainly of poly(methyl methacrylate) (PMMA) powder and methyl methacrylate (MMA) liquid. These components are mixed to form viscous dough, which is applied to bone and used to support the prosthesis. Acting as a grout in the space between the implant and the bone, it is the primary function of the cement to transfer load across this interface and consequently it is instrumental in the load-carrying capacity of the implant–cement–bone construct.

PMMA bone cement is formed by free radical polymerization of liquid monomer, MMA, around PMMA polymer powder. During the polymerization process, the cement undergoes four main phase transformations or stages of cure, which are outlined in Table 1 [**1**]. The progression of the polymerization process is characterized by the continuous increase in viscosity and heat generated from the exothermic reaction. During a joint replacement operation the polymerization reaction of the bone cement is determined by physical examination of the bone cement; it is a very subjective technique that requires a high degree of experience on the part of the orthopaedic surgeon.

Moreover, orthopaedic surgeons have no facility to determine the mechanical properties of the cured bone cement in the operating theatre. Information regarding the mechanical strength of the cement would be beneficial to orthopaedic surgeons, providing quantitative data on the performance of the

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Table 1 Four phases of polymerization for acrylic bone cement

Phase	Description
Mixing	Full integration of the powder and liquid components
Waiting	At the end of which the cement can be handled without sticking to the gloves
Working or dough	The time during which the cement can be manipulated and the prosthesis inserted
Setting	At the end of which the cement is fully hardened

cement from the outset of the total joint replacement, which would be useful if the patient had to be considered for a revision surgical operation as it would provide quantitative evidence as to the mechanism of failure of the joint replacement. Currently, orthopaedic surgeons have to depend solely on bone cement manufacturers, materials scientists, and bioengineers to conduct tests designed by international standard organizations, which are primarily destructive and do not provide the facility to retain the samples post-test for future analysis. These mechanical tests are normally conducted using specimens that are prepared under laboratory conditions. Previous studies have shown that there is little correlation between the quality of bone cement mixed in a laboratory environment and that which is mixed under surgical theatre conditions [**2**, **3**].

It would be more advantageous to have a non-destructive technique that could be used, firstly, to monitor the reaction of the PMMA bone cement as it progresses from viscous liquid to a solid mass of cement and, secondly, to determine the mechanical properties of the cement when it has reached a cured state without jeopardizing the performance of the cement.

Ultrasonic testing uses high-frequency sound energy to conduct various investigations on a wide range of materials [**4–7**]. One of the many possible applications of the ultrasonic technique is to monitor the curing reaction of materials. The acoustic properties of a material are closely related to its mechanical properties; for instance the velocity of sound within a material is dependent upon its density and mechanical properties [**4**, **5**]. During a polymerization reaction these properties are constantly changing. Thus, by monitoring the change in the ultrasonic wave propagation velocity during polymerization it is possible to quantify the state of polymerization.

As with the ultrasonic wave propagation velocity, broadband ultrasonic attenuation (BUA) is also sensitive to the viscoelastic properties of the material. Attenuation may be described as the combined effect of the scattering and absorption of a sound wave. Essentially, polymers act as filters, attenuating the energies associated with the higher-frequency components of broadband sound waves more than those of lower-frequency components. As bone cement polymerizes, transforming from a low-viscosity fluid to a solid, the amount of energy attenuated at each frequency changes. Thus, as the variation in attenuation can be correlated with changing material properties during polymerization, it can be used to monitor the polymerization process.

Viano *et al.* [**5**] presented an ultrasonic technique for the characterization of hydroxyapatite-modified bone cement. Their method used the velocity of sound and BUA to monitor the polymerization reaction of the cement. They used two ultrasound transducers in a through-transmission set-up. The BUA and speed of sound altered markedly during the polymerization reaction and this demonstrated the potential of using the acoustic properties of materials to characterize different types of bone cement.

The aim of this investigation was to show that the ultrasonic pulse-echo technique can be utilized to determine the specific static and dynamic properties for PMMA bone cement in real time. The pulse-echo technique is based on low-intensity pulse ultrasound, which makes the technique both non-invasive and non-destructive. In the first instance, emphasis was placed on monitoring the polymerization reaction of the bone cement, by following how the acoustic characteristics change as a function of setting time. Once the bone cement had set, and its mechanical properties had stabilized, they were also indicated by the measured ultrasonic parameters. The results generated using the pulse-echo technique were compared with results obtained in accordance with ISO 5833 [**8**], which is a standard test method to define setting for acrylic-based bone cements.

2 MATERIALS AND METHODS

2.1 Sample preparation

Three commercially available bone cements were analysed: Palacos® R (Schering-Plough Ltd, UK), CMW® Endurance (DePuy CMW Laboratories, UK) and Simplex P™ (Stryker Howmedica Osteonics Ltd, UK). All cement constituents, mixing aids, and mixing devices were stored in ambient laboratory conditions (temperature, 20 ± 1 °C; relative humidity, 50 ± 2 per cent) for at least 2 h prior to the cement constituents being mixed. All cement constituents were mixed under laboratory conditions according to manufacturer's instructions under the application of a vacuum (-72 kPa) using a third-generation mixing and delivery system (Summit Medical Ltd, UK), after which the dough was quickly and carefully injected into the appropriate specimen moulds [**9**].

2.2 Ultrasonic measurement

For this study, the pulse-echo method was used to determine the velocity of sound by calculating the ultrasonic time of flight or transit time. This method uses a single transducer both to transmit and to receive an ultrasonic pulse. The frequency ascribed to a transducer is the centre frequency, which primarily depends on the backing material. Ultrasonic transducers respond to a broad band or range of frequencies, above and below the central frequency. A low-frequency (2.25 MHz) transducer was used in this study for ultrasonic cure-monitoring analysis, providing greater energy and penetration in the cement. Ultrasonic measurements were conducted in a cylindrical aluminium water bath maintained at room temperature. A PMMA (Perspex®; Plastico, Inc., Tennessee, USA; density, 1190 kg/m^3; molecular weight, 227 000 g/mol; glass transition temperature, 100 °C) sample receptacle measuring 25 mm × 25 mm × 60 mm was positioned on an aluminium block in the centre of the water bath and oriented in such a fashion that two faces were perpendicular to the surface of the transducer. The transducer was connected to a Krautkramer USN 60 (Agfa NDT Ltd, UK) ultrasonic testing system, set to operate in pulse-echo mode. The timing of the polymerization reaction was recorded using a digital stopwatch and commenced upon opening the vial of liquid monomer component. After the required mixing time had elapsed, the bone cement was injected into the receptacle and ultrasonic measurements began as soon as signals were acquired. For the particular testing configuration used in this study, the ultrasonic pulse encounters two opposing walls of the cement receptacle, appearing as two vertical deflections on the display. The display pattern configuration is described as an 'A-scan', where each opposing surface is characterized by a baseline cross-over (Fig. 1). The system allowed the placing of cursors manually on each vertical deflection to determine the time of flight of each pulse. By subtracting the transit time recorded at the first surface from that recorded at the second interface it was possible to calculate the ultrasonic time of flight within the cement. Thus, the velocity of sound within the material was calculated according to

$$c=\frac{2d}{t} \tag{1}$$

Ultrasonic measurements were repeated every 30 s. BUA measurements were performed in parallel with the ultrasonic measurements according to the following procedure. In the first instance, the receptacle was filled with distilled water and a reference signal was recorded. The reference speed of sound through the distilled water at 20 ± 1 °C was 1485 ± 10 m/s, which was in accordance with published data [**9**]. On introduction of the bone cement into the receptacle, a signal was recorded every 30 s throughout the duration of the curing process. A fast Fourier transform was used to obtain the amplitude spectra of the reference and cement signals, $A_{\mathrm{w}}(f)$ and $A_{\mathrm{c}}(f)$ respectively. The attenuation at each frequency point was calculated for each of the bone cement signals using [**5**]

$$S(f)=20\log_{10}\left[\frac{A_{\mathrm{w}}(f)}{A_{\mathrm{c}}(f)}\right] \tag{2}$$

A linear regression was performed for the attenuation data of each cement signal to obtain a range of BUA values. The slope of the fitted line was divided

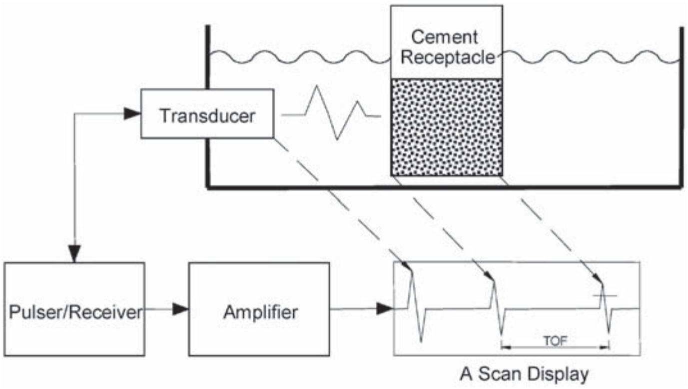

Fig. 1 Ultrasonic cure-monitoring configuration (TOF, time of flight)

by the sample width to obtain a value for BUA in units of decibels per centimetre megahertz. Measurements of the same bone cements were conducted on different days so as not to prejudice the data for any one particular cement type to specific environmental conditions. The final velocity of sound and BUA measurements were repeated after the samples had been stored in atmospheric conditions for 1 month. Three bone cement samples were tested for each type of bone cement.

2.3 Thermal properties

The maximum temperature and setting parameters of each bone cement mix were measured in accordance with ISO 5833 [**8**]. A polytetrafluoroethylene mould was used to contain the bone cement during polymerization, nickel–chromium–aluminium k-type thermocouples were used to measure the temperatures which were recorded using the Labtech Notebook data acquisition software package (Adept Scientific, Ltd, UK). The mixing system, the test equipment, and the constituents of the cement were conditioned in ambient laboratory conditions for at least 2 h before beginning the test. Temperature data were recorded at regular intervals of 1 s for a time span of 30 min. Three bone cement samples were tested for each type of bone cement.

2.4 Rheological properties

Rheological characteristics were measured as a function of elapsed time from start of mixing using an AR 2000 rheometer (TA Instruments Ltd, UK) in dynamic oscillation mode with parallel-plate configuration. Each bone cement mix was prepared as per manufacturer's instructions, and after 45 s from opening the liquid monomer the bone cement was introduced to the rheometer. The plates were brought together and, after excess cement had been removed, the rheometer started and the time was noted. The times between the start of mixing and the beginning of measurements being made by the rheometer were in the range 60–80 s. The rheometer was used in dynamic oscillation in constant-strain mode, with an amplitude of 5×10^{-4} rad at a frequency of 5 Hz. The radius of the upper plate was 20 mm and the gap between the plates was 1 mm. The machine used a solvent trap in the upper plate, filled with liquid monomer to minimize evaporation of monomer from the cement.

The rheometer recorded measurements of dynamic viscosity as a function of time until the viscosity reached approximately 1500 Pa s; the test was then stopped and the equipment cleaned before the cement completely set. All the tests were carried out at a room temperature of 20 ± 1 °C. A total of three bone cement samples was tested for each type of bone cement.

2.5 Density measurement

The apparent densities of the bone cement samples were determined using the water displacement technique, which resulted in determination of the percentage porosity [**8**]. A total of 18 specimens was tested for each bone cement type.

2.6 Compressive properties

The compressive properties of each bone cement mix were determined in accordance with ISO 5833 [**8**] and ASTM F451 [**10**] using a Lloyds materials testing machine (Lloyds Instrument Ltd, UK). The samples were tested under a controlled cross-head speed of 20 mm/s. Each compressive sample was tested to failure; a load versus deformation plot resulted. A total of 18 specimens were tested for each bone cement type.

3 RESULTS

Figure 2 shows the velocity of sound as a function of polymerization reaction through a sample of acrylic bone cement (CMW® Endurance), which is a typical trace for self-curing acrylic bone cement. Each data point corresponds to one digitized signal that has been analysed to calculate the velocity. As the bone cement polymerized, the velocity of sound through it increased significantly near the expected cure time.

Each curve, irrespective of the bone cement type, displayed an initial plateau at approximately 1500 m/s followed by a rapid increase of approximately 1200 m/s between 14 and 18 min, to a second plateau near 2700 m/s. These findings correlate strongly with the results reported by Viano *et al.* [**5**].

Since one of the main aims of this study was to obtain an accurate indication of the working phase for PMMA bone cement using a non-invasive and non-destructive ultrasonic technique, the early stages of polymerization are of most interest. According to Kuhn [**11**], depending on the ambient temperature and bone cement type, the dough or working phase of bone cement ranges between 3 and 8 min. Figure 3 displays the variation in velocity of sound during the proposed working phase for CMW® Endurance, Palacos® R, and Simplex P™ bone cements. All bone cement types displayed similar trends throughout this time period, whereby

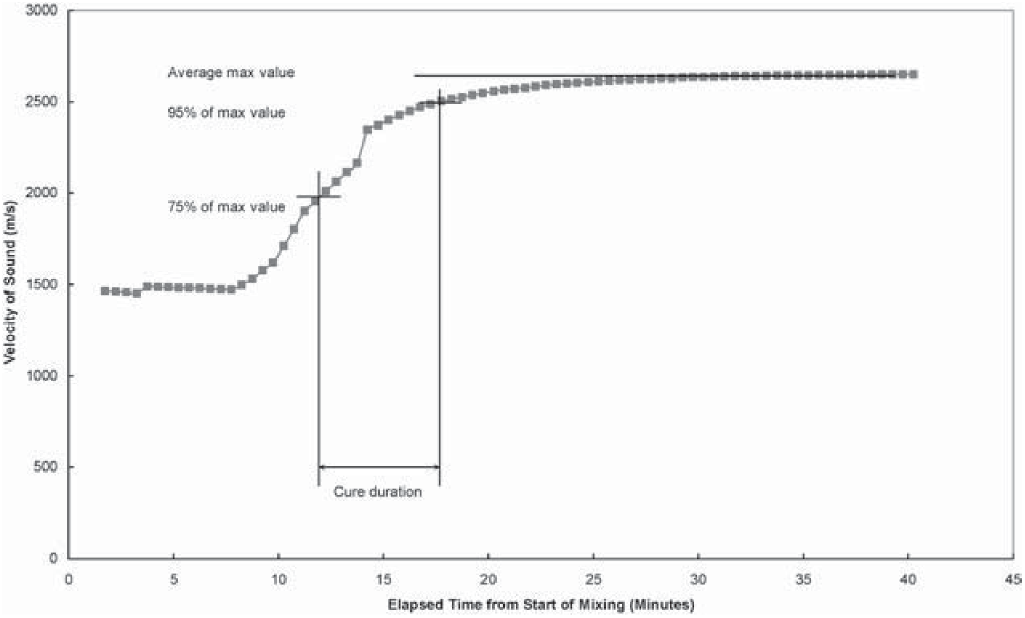

Fig. 2 Velocity of sound for CMW® Endurance bone cement versus elapsed time from the start of mixing, which is a typical trace for all bone cements tested in this investigation**.** The cure time is defined as the time when the velocity has reached 95 per cent of the average maximum value. The cure duration is the interval between 75 per cent and 95 per cent of the average maximum value

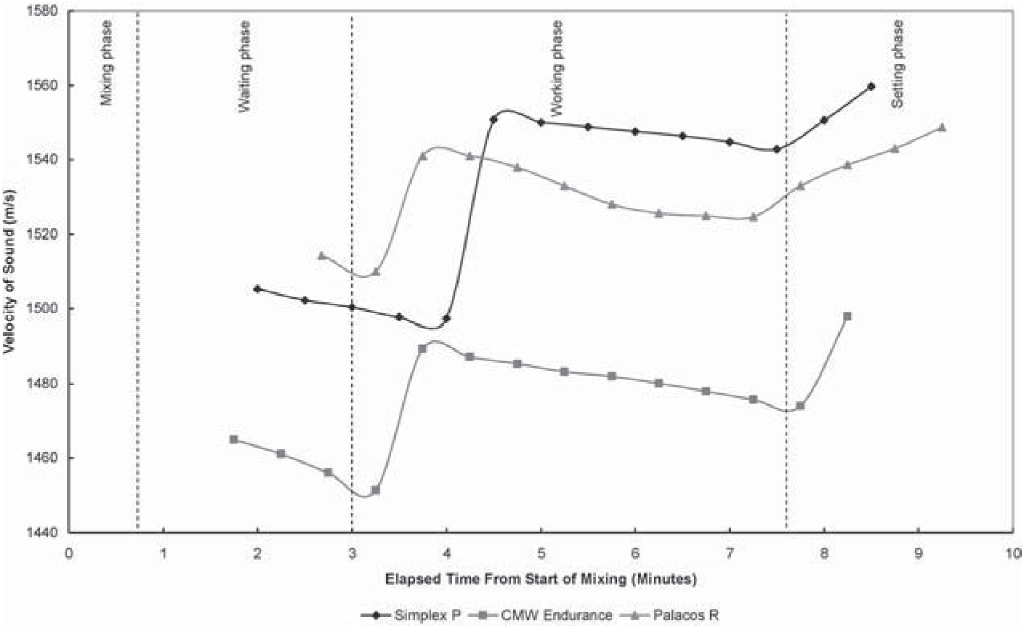

Fig. 3 Velocity of sound versus elapsed time from the start of mixing during the proposed working phase of CMW® Endurance, Palacos® R, and Simplex P™ bone cements

the velocity of sound decreased by approximately 10–20 m/s between 3 and 4 min depending on the cement type; this time point corresponded to the onset of the working phase of the bone cement. Thereafter, the velocity of sound through the respective bone cement sample increased by 30–50 m/s, followed by a gradual decrease in velocity of sound and a subsequent rise that reflected the transition to the setting phase of the polymerization reaction. This shift to the setting phase occurred between 7 and 8 min depending on the bone cement type. These two distinctive points are consistent with the start and end of the working phase of PMMA bone cement, as reported in previous studies [**1**, **11–13**].

To compare the setting times and rates of the polymerization reaction quantitatively, Viano *et al.* defined the *cure time* as the time when the velocity of sound reached 95 per cent of the average maximum value obtained after hardening [**5**]. The *cure duration* was defined as the time difference between 75 per cent and 95 per cent of the aforementioned average maximum value. These characteristics are labelled in Fig. 2. Figure 4 displays a typical graph for BUA versus elapsed time from start of mixing for CMW® Endurance bone cement. This plot shows data from the same sample as the velocity of sound data from Fig. 2. The maximum BUA coincides with the midpoint of transition in velocity of sound. The BUA data shown in Fig. 4 is consistent with those recorded by Viano *et al.* [**5**]. For all samples, BUA had a sharp maximum against a slowly increasing background. It is postulated that the shoulder on the high side of the maximum may imply a second peak at a lower magnitude. This shoulder was a consistent feature in all BUA data. To ensure that these final values for the velocity of sound and BUA were truly characteristic of the fully polymerized cement, the samples were rechecked after being stored for 1 month. The values of the final velocity of sound and BUA were not significantly different from the values measured at the end of the polymerization experiments (p value greater than 0.05). One-way analysis-of-variance tests were performed on the final velocity of sound and BUA measurements and a significant difference identified by a p value less than 0.05.

To assess the validity of using the cure time and cure duration from the velocity of sound versus elapsed time from start of mixing plot (Fig. 2), the polymerization reaction for each bone cement was concurrently monitored in accordance with ISO 5833 [**8**] with each ultrasonic test conducted. Figure 5 shows the exothermic temperature and velocity-of-sound profiles for CMW® Endurance cement versus elapsed time from the start of mixing. The cure temperature and cure time are parameters that were determined in accordance with ISO 5833 [**8**]. Cross-comparing the data generated from the ultrasonic technique and ISO 5833, it can be observed that there is a strong correlation between 75 per cent of the average maximum velocity-of-sound value and the cure time as measured in accordance with ISO 5833 (Table 2). The average cure time measure for CMW® Endurance was 12.40 ± 1.51 min when measured at 75 per cent of the average maximum using the ultrasonic technique, in contrast with 12.18 ± 1.77 min when quantified using the ISO test method. Similar, correlations were noted for Palacos® R and Simplex P™ cements. Furthermore, Palacos® R bone cement is categorized as normal viscosity cement in comparison with Simplex P™ bone cement, which implies that the curing reaction is slower for the latter cement. Table 2 shows that the cure time is greater for Simplex P™ bone cement irrespective of which technique was implemented to monitor the polymerization reaction. The average cure time for Simplex P™ cement was 14.63 ± 2.29 min, compared with 11.95 ± 0.34 min for Palacos® R cement. The differences in the setting characteristics of the bone

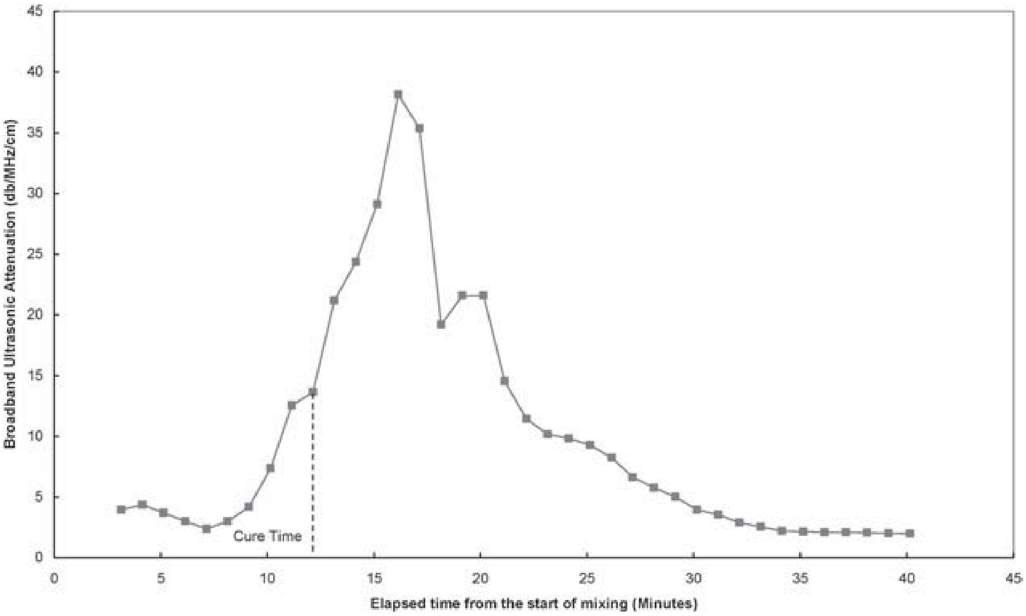

Fig. 4 BUA for a sample of CMW® Endurance bone cement plotted as a function of elapsed time from start of mixing

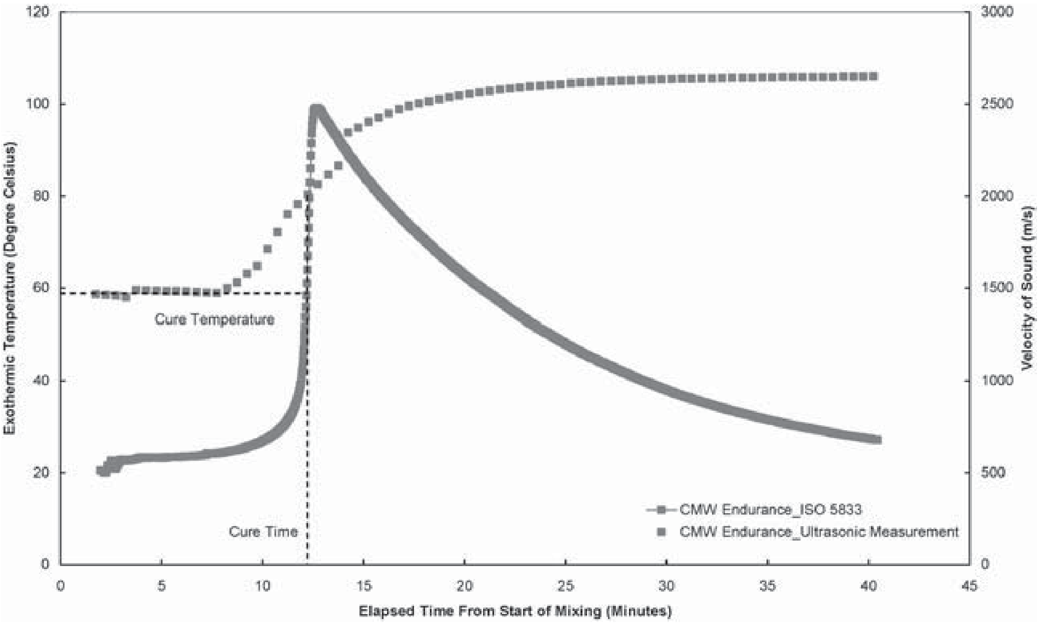

Fig. 5 Exothermic temperature and velocity-of-sound profiles for CMW® Endurance bone cement versus elapsed time from the start of mixing recorded from the same sample of bone cement. The cure temperature and cure time were determined in accordance with ISO 5833

Table 2 Mean values and standard deviations of cure time, cure duration, final velocity, density, and compressive strength that were determined using the through pulse-echo ultrasonic technique

Bone cement	Cure time* (min)	Cure duration (min)	Final velocity (m/s)	Cure time† (min)	Density (g/cm^3)	Compressive strength (MPa)
Endurance	12.40 ± 1.51	4.79 ± 1.56	2654 ± 60	12.18 ± 1.77	1.21 ± 0.01	98.00 ± 4.90
Palacos R	11.95 ± 0.34	4.55 ± 0.63	2586 ± 13	11.70 ± 0.21	1.27 ± 0.01	87.46 ± 4.53
Simplex P	14.63 ± 2.29	4.93 ± 1.59	2655 ± 21	14.61 ± 2.41	1.22 ± 0.01	66.21 ± 11.79

* Cure time as measured using the pulse-echo ultrasonic technique.
† Cure time measured in accordance with ISO 5833 [**8**].

cements investigated in this study are further confirmed by observing the apparent viscosity versus elapsed times from start of mixing graph, which are shown in Fig. 6. The plots for apparent viscosities are typical of those for low- to high-viscosity bone cement, used in the dough form. The rheology results are in accordance with other investigations, which measured the rheological properties of various acrylic bone cements using an oscillating parallel-plate rheometer [**14**]. Farrar and Rose [**14**] observed that the initial rise in viscosity is largely due to swelling of the polymer particles in the liquid monomer; subsequently, polymerization of the monomer also contributes to the increase in viscosity and eventually will dominate.

Figure 7 demonstrates the correlations between the velocities of sound through the bone cements as a function of the densities of the cured samples. It can be observed from Fig. 7 that there is a significant relationship relating the velocity of sound and the density of the cement for all three bone cements investigated in this study ($R^2 = 0.99$). Figure 8 shows the relationship between the velocity of sound and the compressive strength of the cured bone cement sample. It can be noted from Fig. 8 that the relationship between the velocity of sound through the cement and the compressive strength is linear and highly significant ($R^2 = 0.99$). In both cases, as the velocity of sound increased, the density and compressive strength increased proportionately.

Table 2 summarizes the average values of the different parameters that were measured in this study.

4 DISCUSSION AND CONCLUSIONS

Effective ultrasonic characterization of the polymerization reaction of PMMA bone cement may be achieved only by measuring changes in the acoustic

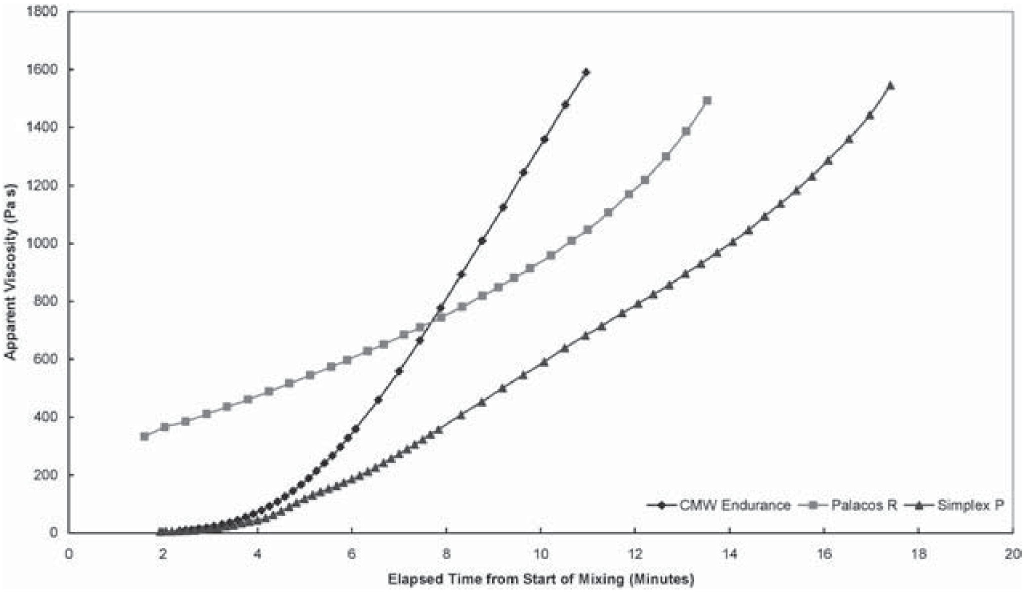

Fig. 6 Apparent viscosity versus elapsed time from the start of mixing for three proprietary brands

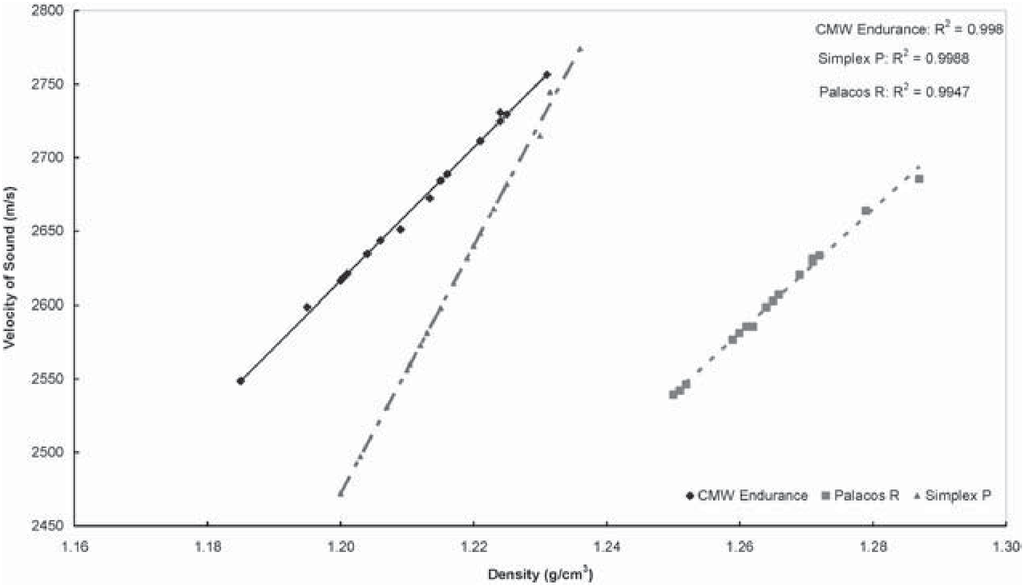

Fig. 7 Velocity of sound through fully cured bone cement versus density for three proprietary brands

properties of the cement that are easily observable. On examination of each ultrasonic trace, a linear decrease in the velocity of sound within the waiting and working phases of the bone cement was clearly evident. The transition of the PMMA bone cement to a workable dough material was apparent by an increase in the velocity-of-sound trace between 3 and 4 min, depending on the viscosity of the bone cement. For Palacos® R and CMW® Endurance the conversion to an injectable material occurred at approximately 3 min, which is typical for normal-viscosity bone cement. For Simplex P™ cement, the transfer from the waiting phase to the dough phase was approximately 4 min. The increase in the velocity of sound during the waiting and working stages was due to a rise in the density of the PMMA cement. During the initial stages of the dough phase there was a characteristic linear decrease in the velocity of sound that may be attributed to the attenuating properties of the emerging molecular structure [**4**]. During this working phase, sound energy is absorbed from interactions with the materials' microstructures causing a delay in the time-of-flight signals. The velocity of sound showed a major increase as the

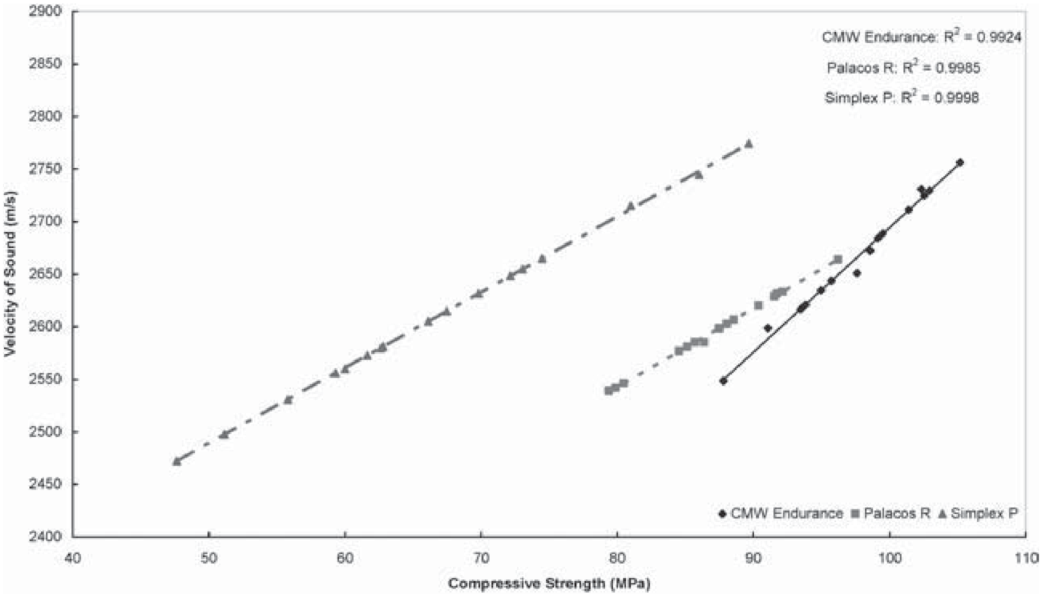

Fig. 8 Velocity of sound through fully cured bone cement versus compressive strength for three proprietary brands

cements went from the working phase to the setting phase, between approximately 7 and 9 min. As the velocity-of-sound trace stabilized within the latter stages of the setting phase, the acoustic properties of the material were no longer changing, thus signifying the end of the chemical reaction.

The effect of attenuation on the velocity of sound was evaluated by monitoring the variation in BUA throughout the curing process (Fig. 4). According to Viano *et al.*, BUA is directly proportional to the number of radicals present during polymerization [**5**]. In the early stages of MMA polymerization, the benzoyl peroxide initiating system generates radicals that react with MMA molecules to initiate polymerization by forming PMMA radicals. At first, the radical concentration is relatively low, resulting in a lower BUA value in the early stages of polymerization; however, as the reaction proceeds throughout the propagation phase, generating more PMMA radicals, BUA increased causing an increase in the velocity of sound. BUA continued to increase up until a point that corresponded to a state containing a large number of PMMA radicals but few joined polymer chains. This stage correlated with peak BUA [**5**]. As the reaction proceeded through the termination phase, the polymer chains joined and BUA decreased, as shown in Fig. 4.

As shown in Table 2, the cure time, defined as the time that it takes from the start of mixing to reach 75 per cent of the final value, showed a strong correlation with the cure times for the different cements measured in accordance with the ISO standard [**8**] for acrylic bone cement resin. This observation does not correspond to the findings of Viano *et al.*; they quoted that the cure time was 95 per cent of the average maximum value of the velocity of sound. However, Viano *et al.* did not compare the cure time measured using the ultrasonic technique with the ISO standard [**5**]. In contrast, Carlson *et al.* [**4**] used the Vicat and Gillmore techniques when they were assessing the feasibility of using an ultrasonic technique to monitor the curing reaction of a calcium-sulphate-based injectable bone cement. Carlson *et al.* used the pulse-echo technique to monitor the setting reaction, and found very strong correlations between 75 per cent of the final velocity of sound value and initial setting time and 95 per cent of the final value and the final setting time.

This investigation was conducted using three different commercial cements, CMW® Endurance and Palacos® R are classed as medium- and high-viscosity cements, while Simplex P™ is a low-viscosity bone cement (Fig. 6) [**12**, **14**]. The viscosity is related to the concentration of polymer molecules [**12**]. Thus, higher-viscosity cements exhibit greater reaction rates and consequently shorter cure durations. As the reaction for a higher-viscosity cement progresses at a faster rate, it should exhibit a higher level of attenuation in the early stages of the polymerization reaction. In the case of Palacos® R this was characterized by the greater rate of reduction in the velocity of sound in comparison with the CMW® Endurance and Simplex P™ cements analysed under similar ambient conditions. For

Palacos® R the average rate of decrease in the velocity of sound was $0.083 \pm 0.004\ \mathrm{m/s^2}$, of the order of twice the values recorded for both CMW® Endurance ($0.050 \pm 0.003\ \mathrm{m/s^2}$) and Simplex P™ ($0.040 \pm 0.003\ \mathrm{m/s^2}$). Conversely, lower-viscosity cements displayed lower reaction rates and thus greater durations of cure [**5**]. This explains the longer setting time exhibited by the velocity traces of Simplex P™ in comparison with CMW® Endurance and Palacos® R, as the curve takes longer to reach the second plateau and to stabilize.

The condition of the cement post-polymerization may be assessed using ultrasonic techniques in addition to mechanical testing. Figures 7 and 8 demonstrate strong linear correlations between velocity of sound and the density and compressive strength respectively for fully cured cement samples. These findings suggest that ultrasonic analysis is a feasible method for determining the mechanical properties of fully cured cement. The final velocity values for CMW® Endurance mixes were generally greater than those recorded for Palacos® R, even though Palacos® R cements are denser. However, Palacos® R may experience higher levels of attenuation than CMW® Endurance cements in the fully cured state, explaining the significantly lower final velocity values. Moreover, the values recorded for final velocity of sound and corresponding compressive strength are similar to those obtained by Viano *et al.* [**5**], suggesting reproducible results, which demonstrates the consistency of ultrasonic analysis.

Traditionally, the polymerization process has been characterized by both physical examination of the bone cement and temperature monitoring during polymerization, as per ISO 5833 [**8**] or ASTM F451 [**10**]. The former technical method for determining the state of polymerization of the bone cement is a much skewed procedure that requires a high degree of expertise on the part of the orthopaedic surgeon. The latter technique is an impractical test method to implement within a hospital environment in terms of material and personnel resources. Implementing the method used to monitor the polymerization of bone cement as per ISO or ASTM standards would require an additional mix of bone cement, which would be assessed concomitantly with the bone cement being used for the joint replacement procedure. Furthermore, an additional mixing system and a theatre nurse would be required to prepare the bone cement. In contrast, through this investigation it has been shown that the ultrasonic pulse-echo technique can provide an objective, reproducible, valid, and non-invasive method for monitoring the polymerization reaction of PMMA cement in real time. Moreover, the ultrasonic pulse-echo technique is cost effective as it utilizes a small sample of cement from the bone cement mix that is actually being used during the surgical procedure, which is mixed using the same mixing device and by the same theatre staff nurse.

The method is relatively easy to use and testing can be made throughout the polymerization reaction without having to move or compromise the cement sample. There are no signs that sound alters the polymerization reaction of the PMMA cement, since the data are in agreement with the temperature data obtained by the ISO standard technique. Moreover, on account of the strong correlation between acoustic and mechanical properties, the pulse-echo technique can be used to determine the density and mechanical properties of PMMA bone cement after polymerization. This association would allow the orthopaedic surgeon the capability to quantify the density and mechanical properties of the cured bone cement in the operating theatre using the pulse-echo technique, in addition to monitoring the polymerization reaction of the cement. It should be pointed out that the mechanical properties could be estimated by determining the density of the bone cement using simpler means such as the water displacement technique; however, this is not likely to be conducted in association with routine procedures [**12**]. The primary application of the pulse-echo technique in this investigation was to characterize the polymerization reaction of acrylic bone cement; the determination of the mechanical characteristics as a function of the acoustic properties of the bone cement was secondary, albeit an interesting finding. Therefore, the pulse-echo test method offers the orthopaedic surgeon the option to implement a technique that could be used under surgical theatre conditions, where the environmental conditions, mixing techniques, and sample thicknesses are often very different from those used in a laboratory scenario, and all these factors are known to influence the performance of the PMMA bone cement.

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APPENDIX

Notation

A_w	water amplitude data point (dB)
A_c	cement amplitude data point (dB)
c	velocity of sound (m/s)
d	receptacle width (m)
t	cement time of flight (s^{-1})
$S(f)$	signal loss (dB)