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Fracture properties of fully cured acrylic bone cement

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The fracture properties of bone cement are strongly influenced by the complex interactions between the residual monomer and components of the media surrounding the bone cement. The aim of this study was to eliminate the influence of the residual monomer by fully curing the cement prior to storage in air, water, lipid or Ringer's solution at room or body temperature for up to 18 months. Subsequent mechanical testing indicated that initially there was a significant increase in the work of fracture values for all the samples stored in the fluid media. With longer-term storage periods a decrease was observed; this was attributed to the process of physical ageing. The removal of the residual monomer eliminated the monomer: lipid interaction, consequently the effect of the storage in lipid was similar to that observed for the other fluid media.

1. Introduction

Acrylic bone cement has a long history of use as a medium for fixing prosthetic components into bone [1]. However, it is recognized that during surgery the cement is inserted into an aggressive environment within the body. As such, it will be subjected to environmental influences that may have an adverse effect on its long-term stability. Changes either within the bone cement or at the bone cement:bone interface are known to contribute to loosening of the implant. The actual mechanism of loosening is not fully understood but it is accepted that both biological and mechanical phases are involved [2, 3].

The results of recent studies have indicated the strong influence that storage temperature and environment can have on the fracture properties of bone cement [4, 5]. Immediately following mixing, bone cement is known to contain approximately 3% trapped residual monomer. The interactions that take place between the monomer and the components of the media surrounding the cement are known to be complex. Measurement of the work of fracture (WOF) values for samples stored in water-based media for time periods of up to 18 months indicated that the water had a plasticizing effect, as a result of which the WOF increased with time. Despite the fact that the lipid, a fat-based solution, could be expected to be a much stronger plasticizer of cement than water, the WOF results for samples stored in lipid, did not show as significant a rise. This may be explained by the complex monomer:lipid interaction [6].

Holding the cement at a temperature above its glass transition point (110 °C) for in excess of 12 h is said to increase the mobility of the monomer sufficiently for continued curing to occur. Such heat treatment can reduce the residual monomer content from 3% to 0.5% [7, 8]. This study undertook to establish more clearly the individual effects of the various media on the fracture properties of bone cement by eliminating the influence of the residual monomer. Following mixing, samples were fully cured to minimize the amount of free monomer remaining in the structure prior to storage in different media at blood or room temperature for specific time periods. The WOF values were then measured.

2. Methods and materials

Simplex P radiopaque bone cement was mixed manually, according to the manufacturer's instructions, at approximately 1 Hz in a non-reactive bowl until the end of doughing time (approximately 4–5 min). The cement dough was then thumbed into a PTFE mould to produce four bars from each batch of cement, 5 mm × 5 mm in cross-section and 220 mm in length. These were cured for 30 min in a press under minimal pressure then removed from the mould and placed in an oven at 115 °C for 15 h. On removal from the oven the samples were allowed to cool in air under ambient conditions for approximately 1 h. They were then placed into one of eight selected storage environments. Four different storage media were chosen: distilled water to simulate a simple liquid environment, Ringer's solution to introduce the physiological salts, Intralipid (an intravenous drip feed solution marketed by KabiVitrum Ltd) which provided a reproducible fat solution to simulate the fat in the bone cavity and air as a control. All the samples were stored in the appropriate media in sterile glass jars maintained at two different temperatures; ambient (21 °C ± 1 °C) and body (37 °C ± 1 °C). The storage time periods

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ranged from 1 day up to 17 months. The storage jars were regularly shaken to agitate the solutions and disperse their contents. Samples were removed from the media and tested at seven time intervals of 1 and 7 days, 3 and 12 weeks and 6, 12 and 17 months.

The 220 mm long bars of cement were cut into test pieces 50 mm long; immediately prior to testing the test pieces were removed from the storage environment and notched. The test procedure involved loading chevron-shaped notched specimens in three-point bending [9]. The notch was introduced into the bar of cement using a purpose made notching jig and a slitting saw with a preset notch depth. The apex of the notch was sharpened using a razor blade, ensuring a sharp crack tip and hence very high stress concentrations at the tip [10]. Approximately 10–12 specimens per environment were then tested in three-point bending on an Instron 1122 test rig, using a constant crosshead speed of 0.5 mm/min. The area of the two fracture surfaces was measured accurately using a Joyce Koebl Magiscan 2A image analyser with a microscaler setup. The work of fracture was calculated by dividing the computed fracture energy by the combined area of the two fracture surfaces.

3. Results

The WOF results for samples of fully cured bone cement stored at two temperatures in different media are presented in Tables I–VIII and shown graphically in Figs 1–4.

It can be seen from Fig. 1 that there was no change in the WOF for samples stored in air over the 500 day time period studied. The results indicated that the samples stored at 37 °C tended to have a lower WOF than those stored at 21 °C but this difference was only slight.

TABLE I WOF results for fully cured bone cement samples stored in air (21 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
Initial	12	237	17	237 ± 11
7 days	11	223	13	223 ± 9
21 days	10	273	18	273 ± 13
84 days	12	252	18	252 ± 11
182 days	11	278	16	278 ± 11
357 days	12	225	21	225 ± 13
497 days	11	282	21	282 ± 14

TABLE II WOF results for fully cured bone cement samples stored in air (37 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	12	218	12	218 ± 8
21 days	10	236	17	236 ± 12
84 days	12	241	18	241 ± 11
182 days	11	233	27	233 ± 18
357 days	13	211	18	211 ± 11
497 days	12	212	28	212 ± 18

TABLE III WOF results for fully cured bone cement samples stored in water (21 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	11	278	24	278 ± 16
21 days	16	401	29	401 ± 15
84 days	11	624	40	624 ± 27
182 days	13	612	48	612 ± 29
357 days	10	642	20	642 ± 14
497 days	11	550	19	550 ± 13

TABLE IV WOF results for fully cured bone cement samples stored in water (37 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	14	350	25	350 ± 14
21 days	10	493	24	493 ± 17
84 days	11	601	33	601 ± 22
182 days	13	505	39	505 ± 24
357 days	11	527	24	527 ± 16
497 days	12	518	45	518 ± 29

TABLE V WOF results for fully cured bone cement samples stored in Ringer's (21 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	11	255	17	255 ± 11
21 days	11	392	42	392 ± 28
84 days	12	609	26	609 ± 17
182 days	11	558	28	558 ± 19
357 days	9	638	49	638 ± 38
497 days	12	520	33	520 ± 21

TABLE VI WOF results for fully cured bone cement samples stored in Ringer's (37 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	12	348	23	348 ± 15
21 days	12	495	29	495 ± 18
84 days	12	570	29	570 ± 18
182 days	13	513	45	513 ± 27
357 days	12	508	19	508 ± 12
497 days	11	524	26	524 ± 17

TABLE VII WOF results for fully cured bone cement samples stored in lipid (21 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	11	245	12	245 ± 8
21 days	12	362	50	362 ± 32
84 days	12	554	40	554 ± 25
182 days	12	553	34	553 ± 22
357 days	10	564	31	564 ± 22
497 days	9	500	58	500 ± 45

TABLE VIII WOF results for fully cured bone cement samples stored in lipid (37 °C)

Storage time	Number of samples	Mean work of fracture (J/m^2)	Standard deviation	95% CI
7 days	14	341	26	341 ± 15
21 days	10	499	37	499 ± 26
84 days	13	516	33	516 ± 20
182 days	11	480	38	480 ± 26
357 days	12	484	34	484 ± 22
497 days	11	443	31	443 ± 21

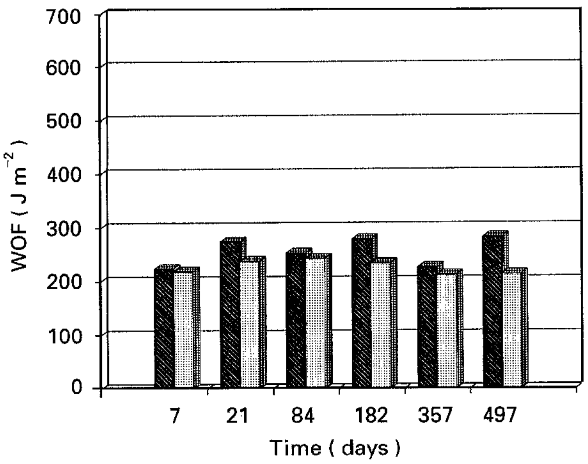

Figure 1 WOF results for fully cured cement in air at 21 °C (▩) and 37 °C (▦).

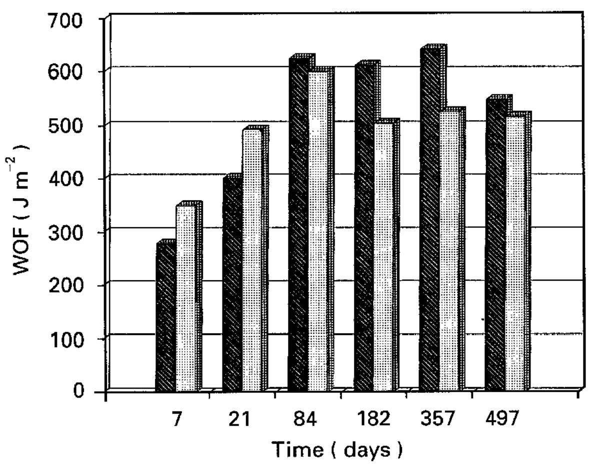

Figure 2 WOF results for fully cured cement in water at 21 °C (▩) and 37 °C (▦).

Figs 2–4, for the fluid media, show a dramatic increase in WOF over storage time, with a maximum reached at 84 days for samples stored at both 21 °C and 37 °C. The WOF for the samples stored at 21 °C then remained steady until 497 days storage when there was a decrease in the WOF. In contrast, the WOF of samples stored at 37 °C reached a peak at 84 days and subsequently experienced a decrease at 182 days to a constant value which remained the same until the maximum storage period of 497 days.

The results show that for storage times up to 21 days in the three fluid media, the WOF was higher for samples stored at 37 °C than for those stored at 21 °C. After 84 days storage, however, this trend was reversed and samples stored at 21 °C had a higher WOF than those at 37 °C. By 497 days samples stored at both temperatures had similar WOF values.

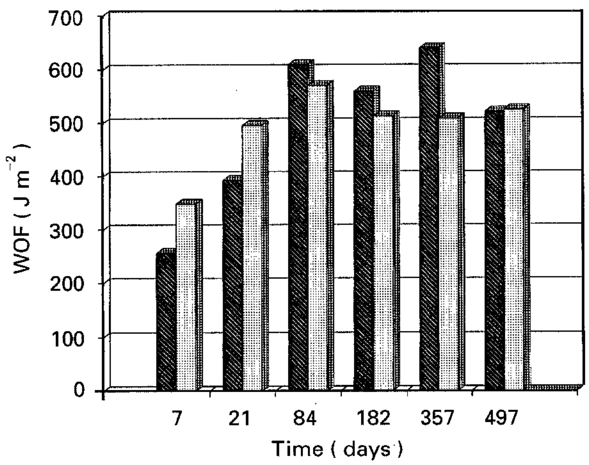

Figure 3 WOF results for fully cured cement in Ringer's solution at 21 °C (▩) and 37 °C (▦).

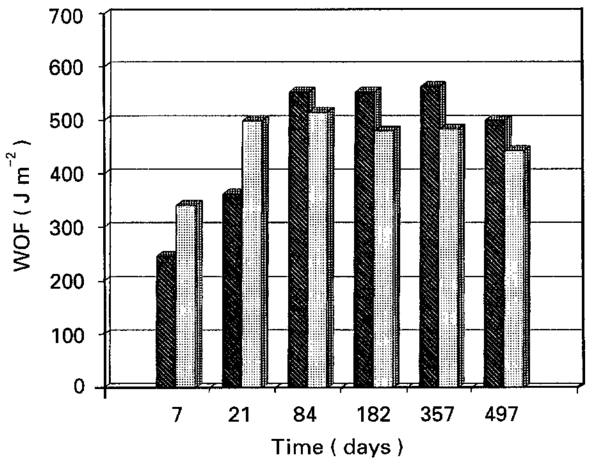

Figure 4 WOF results for fully cured cement in lipid at 21 °C (▩) and 37 °C (▦).

4. Discussion

Storage of samples in the fluid media resulted in a significant increase in the WOF when compared to samples stored in air. Specimens stored in water and Ringer's solution had similar WOF values at each of the time periods studied. In contrast, samples stored in lipid gave consistently lower WOF values than for the two water-based media.

The graphs show that the most significant changes in WOF occurred within the first few days of storage (up to 21 days). The variation in WOF with longer storage periods was shown to be much more gradual.

Storage of fully cured samples in the fluid media was shown to have the same plasticizing effect as that observed with the normal cement [4, 5]. However, it was found with fully cured cement, that the discrepancy between the WOF for lipid-stored samples and that for water-stored samples was smaller than it was for samples of normal cement. Removal of the residual monomer as a variable from within the cement has eliminated the effect of the monomer–lipid interaction, which was observed with the normal cement. Hence, for the fully cured cement, the effect of storage in lipid would be similar to that of storage in water and Ringer's.

For storage periods of up to 12 weeks, it was found that samples of fully cured cement which were stored in the fluid media at 37 °C had higher WOF values than samples which were stored at 21 °C. This was the reverse of the effect observed with the normal cement, where the samples stored at 37 °C had the lower WOF. It is postulated that since the residual monomer had been removed from the fully cured cement, there was no longer competition between increased monomer loss and increased environmental ingress at the elevated storage temperature. The only effect of storage at 37 °C, as opposed to 21 °C, was to increase environmental ingress into the fully cured cement, thus increasing the WOF.

With longer storage periods (over 12 weeks) there was a significant decrease in the WOF which occurred earlier for samples stored at 37 °C than for samples stored at 21 °C. This decrease in WOF occurred after 6 months and 17 months for samples stored at 37 °C and 21 °C, respectively. The same effect was seen to a lesser, yet still significant, extent in the normal material after storage for 2 years at both 21 °C and 37 °C [12].

These long-term decreases in the WOF could be due to a process termed physical ageing [11]. PMMA is a glassy polymer, which is essentially a solidified supercooled liquid. The free volume (V_f) of the material is therefore greater than it would be at equilibrium. As the material is cooled from above its glass transition temperature (T_g) to room temperature, the free volume decreases, but remains greater than the equilibrium value. Physical ageing involves the continued slow decrease of the free volume towards the equilibrium value. As the free volume decreases, so the polymer chain mobility also decreases, and the material becomes more brittle. The rate of physical ageing increases with elevated ageing temperatures, and is also related to the thermal history of the polymer. Since the fully cured material was heated beyond its glass transition temperature (115 °C) for over 15 h, and the normal material only reached the temperature of the polymerization exotherm (approximately 100 °C) for several minutes, it is likely that the fully cured material would be more susceptible to physical ageing than the normal material. Storage of the cement at 37 °C as opposed to 21 °C would also increase the rate of physical ageing, thus the cement stored at the higher temperature would exhibit brittle tendencies earlier than the cement stored at 21 °C. The WOF results from this study support both these hypotheses, thus physical ageing of the cement is offered as an explanation of the deterioration in the WOF after long-term storage in the fluid media. This effect was not observed with the air-stored cement as it failed in a completely brittle manner. It has been shown, using impact tests, that when PMMA fails in a brittle manner, changes in the free volume have no effect on the impact strength of the material. If, however, the material fails in a ductile manner (by increasing the test temperature), then physical ageing and free volume changes once again become important [11].

Significantly reducing the residual monomer content in the bone cement to 0.5% has allowed the complex interactions between bone cement and the different storage media to be more clearly understood. It has been shown that the individual storage media and temperatures have significantly different effects on the fracture behaviour of bone cement. The results indicate the complexity of the interactions expected to take place *in vivo* with the 3% monomer initially trapped within the cement.

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