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The effect of post-curing chemical changes on the mechanical properties of acrylic bone cement

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Total joint replacement is a procedure which gives pain relief and renewed mobility to over 50 000 people each year in the UK alone. While offering new hope to many of these people, approximately 10% of these prostheses fail within 10 years. It is thought that cement fracture could be one cause of the failure of the implant. This study was primarily concerned with the effect of storage environment and time period on the work of fracture of Simplex P bone cement. It was found that the storage conditions had a significant influence on the work of fracture of bone cement. In particular, storage at body temperatures embrittled the cement, while storage in fluid media had a plasticizing effect. These trends were related to post-curing chemical changes within the cement mass, specifically the absorption of low molecular mass species from the storage environments, and the leaching of residual monomer from the cement.

1. Introduction

Aseptic loosening remains the major long-term problem with total joint replacement. The reasons for this loosening are still not fully understood, although it is generally accepted that it involves both mechanical and biological contributions. It is the mechanical phase of loosening with which this study was concerned. In particular, fracture of the bone cement mantle, a feature often associated with aseptic loosening.

In vivo fracture of bone cement has been well documented in the literature [1–8], both in terms of gross catastrophic fracture of the whole cement mantle and as microfracture of the intrusions into the adjacent bone. There is also considerable literature on the fracture properties of acrylic bone cement [9–16]. Yet it is obvious when reviewing this literature that there had been no standardization of the fracture test procedures. Several different test methods were used in the studies. There was a lack of data on the fracture properties after long-term storage, and the individual influences of isolated components of the physiological environment had not been evaluated. The various workers had not tried to ascertain if there were any differences between storage at elevated temperatures as opposed to storage at room temperature, or between storage in the various fluids used (water, Ringer's solution and bovine serum). Considering the relatively high fat content in the bone cavities which the cement is expected to interface with, it was surprising that there had been no work to evaluate the effect of storage of cement in lipid solutions.

The aims of this project were to establish the effect of ageing environment and time period on the fracture behaviour of Simplex P bone cement, and to relate these effects to any chemical changes occurring within the cement mass. The fracture behaviour of the cement was characterized by work of fracture (WOF) tests, which were based on a test devised by Tattersall and Tappin in 1966 [17]. The ageing conditions were chosen to simulate the individual components of the physiologically environment so that the influence of each variable could be ascertained.

2. Materials and methods

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 bars of cement with dimensions 5 mm × 5 mm cross-section and 220 mm in length. After curing for 30 min in a press under minimal pressure, the cement bars were removed from the mould and placed into one of the selected storage environments. Eight different storage environments were used, these consisted of four different storage media and two temperatures. The media were as follows; distilled water to simulate a simple liquid environment, Ringer's solution to introduce the physiological salts, Intralipid which provided a reproducible fat solution to simulate the fat in the bone cavity, and air as a control. These media were stored in sterile glass jars and maintained at two different temperatures; ambient, 21 °C, and body, 37 °C. The storage times studied ranged from 1 day up to 18 months for the cement.

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After storage for the required time period, the bars of cement were cut into 50 mm test pieces. Immediately prior to testing the test pieces were removed from the storage environment and notched. The apex of the notch was sharpened using a razor blade, which ensured a sharp crack tip and hence very high stress concentrations at the tip. Approximately 10–12 specimens per environment were then tested in slow three-point bending under ambient conditions (in air at 21 °C). The notched specimens were loaded on an Instron 1122 test rig using a constant cross head speed of 0.5 mm/min. The load versus displacement graph was integrated to give the area under the curve. This area was then converted into the total work done in fracturing the specimen, or the fracture energy. The WOF was calculated by dividing this fracture energy by the combined area of the two fracture surfaces.

Samples for environmental ingress studies were mixed and cast using the same protocol as that for the WOF test specimens. The specimens were weighed immediately prior to storage and periodically during immersion in one of the eight storage environments using the methods described in ISO 4049 (1988) [18] and ASTM F451-76 (1976) [19].

The residual monomer content of the bone cement was determined using a Pye Series 104 gas chromatograph with flame ionisation detection (FID). The detector temperature was 250 °C and the oven temperature was 150 °C. Nitrogen carrier gas was used at a flow rate of 45 cm^3/min through a column containing a stationary phase of 5% FFAP coated onto Chromosorb. Chlorobenzene was used as the solvent for the polymer, and the internal standard was hexane. A Hewlett Packard HP3390A Integrator was used to calculate the areas of the peaks on the chromatograph trace. A sample of approximately 0.3 g cement was weighed out and the weight recorded accurately. The cement sample was then added to 25 ml of the hexane laced solvent and dissolved by gentle warming at 35 °C for 12 h followed by sonication in a water bath at 70 °C for 20 min. The solutions were then left for 12 h, to allow the barium sulphate particles to settle out of solution. A 0.0004 ml sample of each cement solution was injected into the chromatograph, and the relative peak areas from the trace were recorded. These areas were then converted into percentage residual monomer contents.

3. Results

Figs 1 and 2 show the WOF results for specimens stored at 21 °C and 37 °C, respectively. The environmental ingress of the four storage media at 21 °C and 37 °C are shown in Figs 3 and 4, respectively. Figs 5 and 6 show the residual monomer contents of samples stored in the various environments for 3 and 18 months, respectively.

4. Discussion

4.1. WOF Results

It has been shown that the WOF of samples stored in air decreased over the 18 month time period studied.

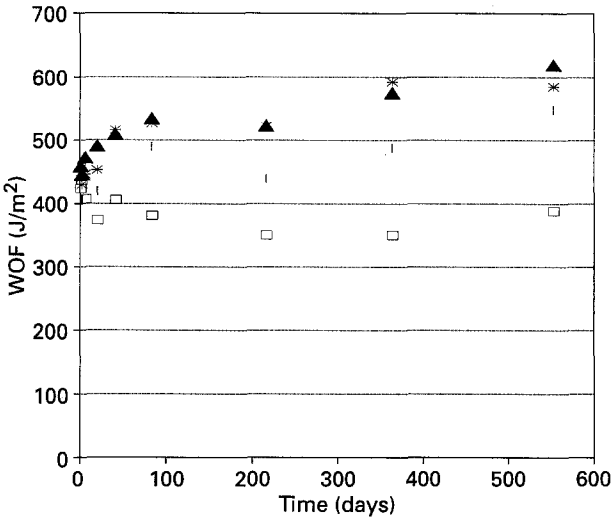

Figure 1 Work of fracture results for bone cement samples stored at 21 °C (□ air; ▲ water; * Ringer's; 1 lipid).

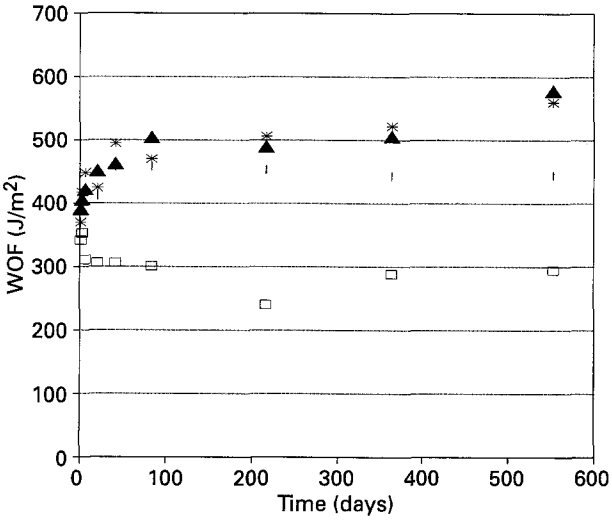

Figure 2 Work of fracture results for bone cement samples stored at 37 °C (□ air; ▲ water; * Ringer's; 1 lipid).

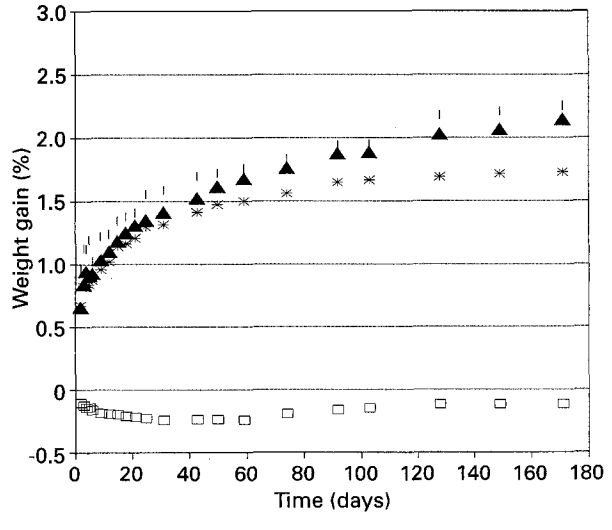

Figure 3 Environmental ingress results for bone cement samples stored at 21 °C (□ air; ▲ water; * Ringer's; 1 lipid).

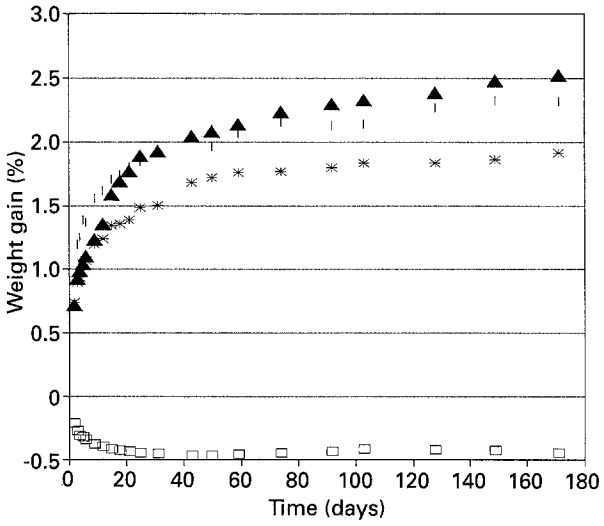

Figure 4 Environmental ingress results for bone cement samples stored at 37 °C (□ air; ▲ water; ∗ Ringer's; 1 lipid).

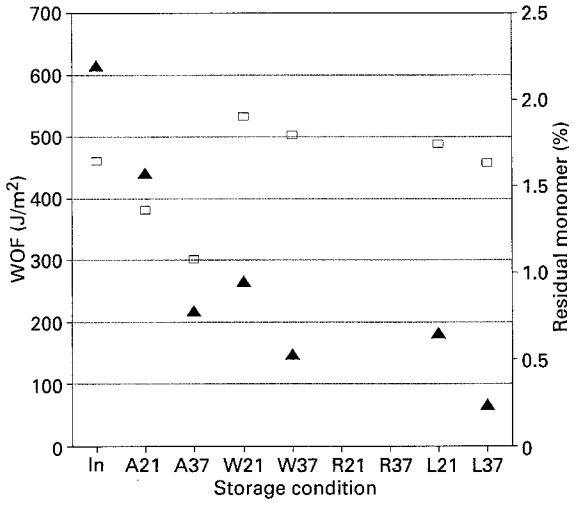

Figure 5 Work of fracture results versus residual monomer contents for bone cement samples after storage for 3 months (□ WOF; ▲ GC).

This decrease was attributed to the loss of residual monomer, which is known to act as a plasticizer on the cement. The plasticizing effect of residual monomer on polymethylmethacrylate has been reported by many authors [20–22], and Caul *et al.* [22] showed a direct relationship between residual monomer content and elastic modulus of dental acrylics.

The effect of storing samples in water was to increase the WOF with time. This increase was attributed to the plasticizing effect of the ingress of water on the cement. There was no significant difference between the WOF values for water and those for Ringer's. So the physiological salts appeared to have no effect on the fracture behaviour of bone cement. The increase in WOF was due solely to the plasticizing effect of the ingress of the water. Several other authors have also reported on the plasticizing effect of the ingress of water into bone cement [13, 15, 21, 23].

The effect of storage in lipid was again to increase the WOF values, although not as significantly as the two water-based media. One would expect the lipid to be a stronger plasticizer of polymers than water, however, this was not the case with bone cement. It is known that the monomer is a powerful lipid solvent, and it is thought that this monomer–lipid interaction was responsible for the WOF values being lower than expected.

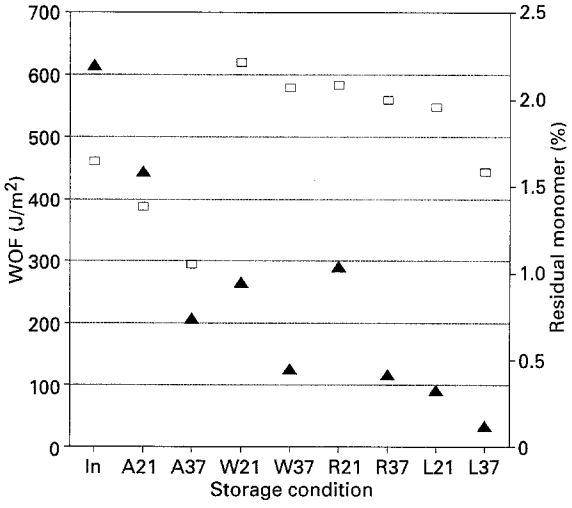

Figure 6 Work of fracture results versus residual monomer contents for bone cement samples after storage for 18 months. (□ WOF; ▲ GC).

In all four storage environments the WOF for samples stored at 37 °C was lower than for those stored at 21 °C. This result was not as expected. It was thought that the higher temperature would increase the diffusion and mobility of the storage media and thus increase the environmental ingress, which would in turn increase the WOF. However, the higher temperature may also have increased the diffusion and mobility of the residual monomer, thus making it easier for the monomer to either leach into the storage medium, or for continued curing to occur. Thus there would appear to be some competition between environmental ingress and residual monomer content. Haas *et al.* [24] showed that regardless of polymerization temperature, samples which were aged at 37 °C for several hours had lower indentation and higher recovery values than those aged at 21 °C for a similar time. This would suggest that samples aged at 37 °C have a higher modulus and hence a lower resistance to crack growth than samples aged at 21 °C, which supports the results obtained in this study. The results of this study would, therefore, indicate that at 37 °C the increased mobility of the monomer had a greater overall effect on the WOF than increased mobility of the storage media. Watson *et al.* [15] found similar results to those in this study, that with storage in both air and water, samples which were stored at 37 °C had a lower WOF than those stored at 21 °C.

4.2. Environmental ingress results

Samples of cement which were stored in air lost weight with time, which was probably due to the loss of residual monomer from within the cement. The slight weight increase with long-term storage was attributed to the samples absorbing water vapour from the atmosphere.

Samples stored in the three fluid media all gained weight with time, indicating that environmental ingress was occurring. Within experimental error there appeared to be no difference between the weight gains for the fluids, thus indicating that the fluid uptake was the same for all of the three liquid media. It was also apparent that there was little difference between the environmental ingress for samples stored at 37 °C and those stored at 21 °C. Using a diffusion coefficient of 2×10^{-8} cm^2 s^{-1} (an average of the diffusion coefficients at 21 °C and 37 °C), Braden [25] showed that for specimens 5 mm thick 99.9% saturation would occur after approximately 120 days in water. This is in good agreement with our results, as the environmental ingress graphs (Figs 3 and 4) began to stabilize after approximately 140 days.

4.3. Gas chromatography results

The residual monomer content was highest for the sample tested immediately (30 min) after curing, followed closely by the samples stored in air. Storage of samples in lipid resulted in the lowest residual monomer content of all the media, with the monomer contents of samples stored in water and Ringer's fallling between the values for air and lipid. There was no difference between the monomer contents of samples stored in water and those stored in Ringer's. This implied that the monomer, which is known to be a powerful lipid solvent, leaches easily into the lipid medium, but leaches less readily into air and the two water-based media. The samples which were stored in lipid had an initial residual monomer content of 2.2%, and within 3 months of storage at 37 °C this had decreased to value of approximately 0.2%. This suggests that virtually all the residual monomer in cured cement could be leached out into the fat within the joint cavity by a few months after insertion. As discussed above, samples which were stored in water lost more residual monomer than those which were stored in air. This is consistent with the work of Basker *et al.* [26] who suggested that this was not due to the leaching of the monomer into the water, but instead due to the continued curing of the water stored cement.

It has also been shown that there was no difference between the monomer contents of samples stored for 3 months and those stored for 18 months in both air and water. However, for samples stored in lipid the monomer content after storage for 18 months was less than that after 3 months. These results showed that in air and water, the monomer leached out of the cement over the first few weeks, with no further leaching after that period. In lipid the monomer was still continuing to leach out from the cement after storage for over 3 months. This observation supports that discussed previously, that more monomer leaches into lipid than into air or water. It has been shown by various workers that methylmethacrylate monomer can be detected in the blood of patients undergoing joint replacement operations. Albrektsson [27] and Willert *et al.* [28] have shown that the residual monomer has the greatest affinity for tissues which are rich in fat cells, due to the fat solubility of the monomer.

In all four of the storage media, samples which were stored at 37 °C had a lower residual monomer content than those stored at 21 °C. Although the solubility of methylmethacrylate in water decreases slightly with an increase in temperature, it is very unlikely that it would have decreased below the saturation point. Thus the only effect of storage at the higher temperature would have been to increase the diffusion and mobility of the monomer, which in turn would have either allowed continued curing of the cement, or made it easier for the monomer to leach into the storage media.

5. Conclusions

The post-curing chemical changes occurring within bone cement have a significant influence on the fracture behaviour of the material. As with dental acrylics, the mechanical properties of acrylic bone cement are influenced by the leaching of low molecular mass species from within the cement mass, and by the absorption of other low molecular mass species from the environment surrounding the cement.

Storage of bone cement at physiological temperatures as opposed to laboratory temperature was shown to have a significant influence on the post-curing chemical changes within bone cement and hence a significant effect on its fracture behaviour. Samples of cement stored in air at laboratory temperature had WOF values 25% higher than samples stored in air at body temperature. For samples stored in the fluid media, those stored at laboratory temperature had WOF values up to 20% higher than samples stored at physiological temperatures.

The physiological salts have been shown to have no effect on the post-curing chemical changes which take place within bone cement, and hence have no effect on its fracture behaviour.

Storage of samples in lipid was found to allow easier leaching of the low molecular mass species from within the cement mass, which resulted in a lower WOF than that obtained when samples were stored in water. Samples of cement which were stored in lipid had WOF values which were generally 10% lower than for samples which were stored in the water-based media.

Many of the previous studies which have characterized the post-curing chemical changes and the mechanical properties of bone cement were performed under laboratory conditions, in air at room temperature. However, this study has shown that the *in vivo* environment significantly influences both the chemistry and the mechanical behaviour of bone cement. Hence it is essential that future studies attempt to replicate the physiological situation as closely as possible.

Acknowledgements

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