

The setting of gypsum plaster

Part II *The development of microstructure and strength*

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The setting process of gypsum plasters has been followed using strength testing, acoustic techniques and scanning electron microscopy. Gypsum plasters were found to set in three stages: formation of the calcium sulphate dihydrate crystal matrix followed by relief of internal stress, and finally evaporation of excess water. The α -calcium sulphate hemihydrate set faster than the β -form, giving a higher initial and final set strength. The set α -plaster consisted of relatively short stubby dihydrate needles with a greater degree of intercrystalline bonding, resulting in greater strength. The microstructure of set α -plaster appeared to be the result of a slower precipitation rate of dihydrate during the hydration reaction of hemihydrate.

1. Introduction

Calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, hydrates to calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in dilute suspensions, or in the form of pastes which set to hard masses [1]. The hardened paste is not a compact solid, but a highly porous material with a relatively large internal surface, consisting of interlocking crystals in the form of plates and needles [2].

The microstructure of hardened gypsum pastes affects most of the physical and engineering properties of the material and, in particular, its rigidity, which is due to the skeleton of interlocking crystals [3]. The strength will depend on:

- (i) the size and shape of component crystals;
- (ii) the strength of the bond between the crystals;
- (iii) impurities which may form part of the crystals, hardening them or predisposing them to fracture;
- (iv) the amount of empty space in the set mass will be determined by the amount of excess water used for mixing. It has been demonstrated [2, 3] that strength increases as the water/plaster (W/P) ratio is reduced. In practice, the water content is dependent on the nature of the plaster [4], and if this could be reduced, the strength could be significantly increased.

Hemihydrate has two forms; α and β , and previous workers [5, 6] agree the α -form produces a "set-plaster" which is stronger than that produced by the β -form, but disagree on which form sets most rapidly.

The present work investigated the setting processes by use of strength testing, acoustic techniques and scanning electron microscopy. Differences in the setting rates of the α - and β -plasters were examined with a view to correlating the microstructure with the mechanical properties.

2. Materials

The hemihydrates were commercial products obtained from British Gypsum and the results of their

characterization have been reported in a previous paper [7]. It was found that both forms contain 97.6 wt % $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ and 2.4 wt % CaSO_4 , with impurities present in quantities of less than 0.2 wt % each. The differences between the two forms was due to different production processes resulting in materials with distinctly different physical conditions and not due to different crystalline phases. Dry decomposition methods give the β -hemihydrate which is a poorly crystalline, porous product with particles consisting of randomly orientated small crystallites, whilst the α -form is produced by hydrothermal methods and consists of larger, well-formed crystals.

3. Experimental procedure

3.1. Measurement of mechanical properties

The mechanical failure of plasters used for medical purposes has been shown to be due to tensile stresses [8, 9] which are generated by bending [8]. The three-point bend test was chosen because it was the closest approximation to the mode of failure. The test is simple and errors can be reduced by statistically analysing a large number of samples (typically 20 or more [10]). As in the previous paper [7] the plaster slurries were mixed at a W/P ratio of 0.6. The test specimens were prepared in the form of bars (50 mm \times 10 mm \times 10 mm) cast in a silicone rubber mould. Prior to testing the specimens were kept at constant temperature and humidity (30 °C, 63% RH) in a humidity cabinet. Specimens for "wet testing" were prepared in the same manner, except a polyethylene film was placed on the top of the mould to prevent moisture loss after casting. When these specimens were removed from the moulds they were immersed in a saturated solution of dihydrate until required for testing. The specimens were tested on a three-point bend rig with the following conditions: (i) distance between

lower rollers, $L = 40$ mm; (ii) loading rate of 36 N min^{-1} .

3.2. Examination of microstructure

3.2.1. Scanning electron microscopy

Samples were prepared by cutting a section (> 2 mm) from the fractured surface of the broken bend test specimen. This was then washed with ethanol to remove the aqueous solution and "arrest" the hydration process. Each sample was mounted on an aluminium stub and gold-coated before being examined under a Jeol T-200 SEM.

3.2.2. Acoustic emission

The experimental apparatus is shown in Fig. 1, but was used without the pulsed transducer. The plaster slurry was poured into the silicone rubber mould; the electrical signal from the detector transducer was then amplified and analysed by an electronics package. Total system amplification was set at 99 dB and the threshold for the event measurements was set at 18 dB. Ring counts and events [11] were measured over 1 min periods and the results were quoted as rates.

3.2.3. Acousto-ultrasonic testing [12]

The apparatus is as shown in Fig. 1 with the pulsed transducer transmitting a continuous signal of 1 Hz frequency. Total system amplification was set at 93 dB, with a threshold for the event measurements set at 24 dB. Ring counts, events and the amplification distribution of events were measured over 1 min periods. Because each pulse is detected as one event, the results were quoted as ring counts per event (or pulse) and as the average amplitude of events.

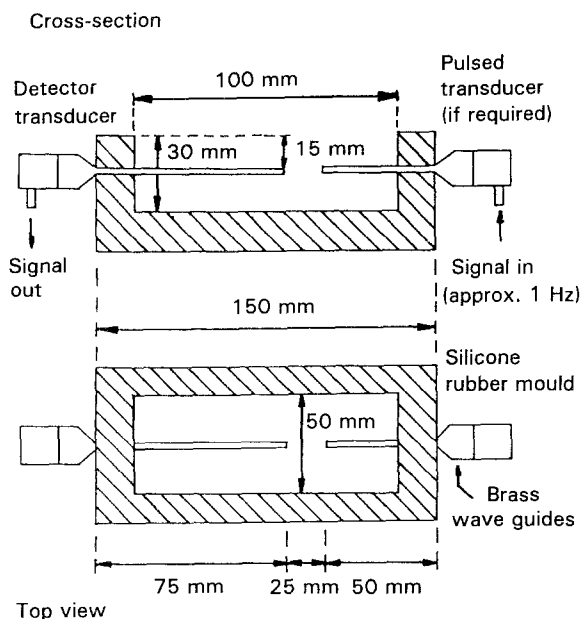


Figure 1 Experimental apparatus for the acoustic emission and acousto-ultrasonic testing of setting gypsum plasters.

3.2.4. Porosity measurements

The open porosity of set gypsum plasters was determined from the amount of toluene absorbed by a block of set plaster. The test specimens were in the form of cubes ($18 \text{ mm} \times 18 \text{ mm} \times 18 \text{ mm}$) cast in stainless steel moulds. The samples were prepared and treated in the same manner as the strength test specimens (Section 3.1). The specimens were weighed before and after vacuum impregnation with toluene. Finally, they were re-saturated and weighed immersed in toluene; from this the open porosity was calculated.

4. Results and discussion

4.1. Development of strength

The strength development during the setting of α - and β -hemihydrates is shown graphically in Fig. 2. The development of strength appears to be a three-stage process:

- (i) an initial rapid build-up of strength reaching a maximum after $1-1\frac{1}{4}$ h;
- (ii) a drop in strength between $1\frac{1}{4}$ and 2 h, with a fall to approximately 80% of the initial maximum strength reached in stage (i);
- (iii) finally, a further increase in strength over the next 15–20 h reaching a limiting value at approximately twice that of the initial strength in stage (i).

In the previous study [7] of the hydration chemistry of hemihydrates, it was shown that the hydration reaction is completed after approximately 60 min. Scanning electron microscopy (Figs 3 and 4) show that an interlocking dihydrate crystal matrix had been formed by the precipitation of dihydrate during the hydration reaction corresponding to the first stage.

Three explanations have been considered to account for the loss of strength observed in stage (ii). Firstly, once a specimen is cast, the specimen starts to lose water by evaporation. This occurs initially from the exposed surface and could possibly result in shrinkage of a surface layer, with the formation of microcracks leading to reduced failure stress. The second possible reason is that with a large amount of heat generated by the hydration reaction (temperatures up to 30°C have been generated adiabatically) thermal gradients may be produced across the specimen. Because the interior and exterior would expand

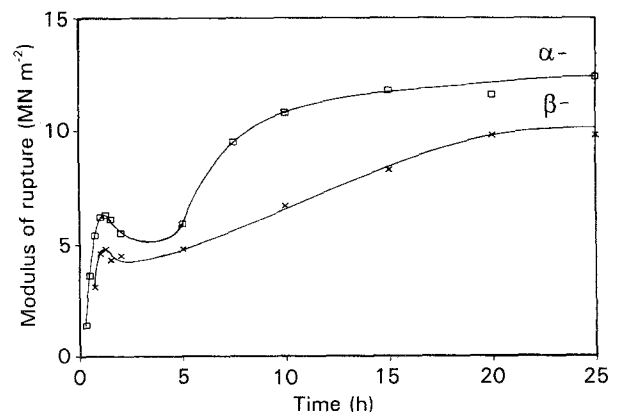


Figure 2 The development of strength as the hemihydrate sets.

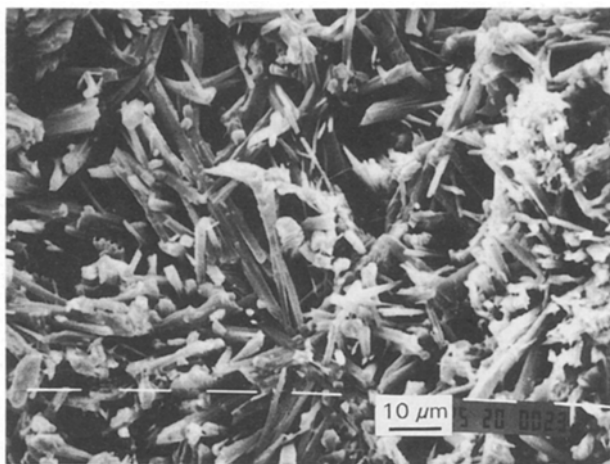


Figure 3 Scanning electron micrograph of the solid phases present in a partially reacted mixture of α -hemihydrate and water after 60 min (W/P ratio = 0.6).



Figure 4 Scanning electron micrograph of the solid phases present in a partially reacted mixture of β -hemihydrate and water after 60 min (W/P ratio = 0.6).

by different amounts this could lead to surface microcracking. Finally, during the growth of dihydrate needles it is possible that internal stress could be built up due to the crystals from different growth centres “pushing” against each other. When the specimens were tested the internal stress would be relieved, resulting in a lower applied stress for failure and as a consequence a lower strength.

Stage (iii) of the setting process is due to the loss of lubricating solution between the dihydrate crystals as the specimen dried out. The remaining dihydrate would then precipitate from solution between the needles, “cementing” them together and making the structure rigid. Evidence to support this idea was sought from a comparison of the strength tests of wet and dry plaster. Wet plaster has been shown to creep near the breaking strength, whilst dry plaster acts as a brittle material [1]; thus, the role of the excess water as a lubricant seems clear.

The strength of the “wet” test specimens, produced by immersion in a saturated solution of dihydrate, was

determined by a similar manner. The “wet” strength of the setting plasters is shown in Fig. 5, with both curves showing an initial strength increase to a maximum followed by a decrease. After this decrease the strength remains constant. This suggests that surface microcracking due to shrinkage is not responsible for the observed strength decrease and it is probably due to thermal gradient microcracking or internal stress. No final increase in strength was observed due to the prevention of bulk drying.

4.2. Microstructural formation

Scanning electron microscopy of the developing structure shows dihydrate crystals to have nucleated and grown on the hemihydrate particles (Fig. 6). The difference between the set plasters of the two hemihydrate forms (Figs 3 and 4) is one of the dihydrate’s crystal habit. The set α -plaster consisted of a mass of interlocking, stubby dihydrate needles, whilst the set β -form had a microstructure of interlocking, fibrous and branching needles.

The porosity measurements of the set plasters for the two forms, each at a W/P ratio of 0.6, indicated that a constant W/P ratio gave a constant porosity, with both giving a porosity of approximately 48%.

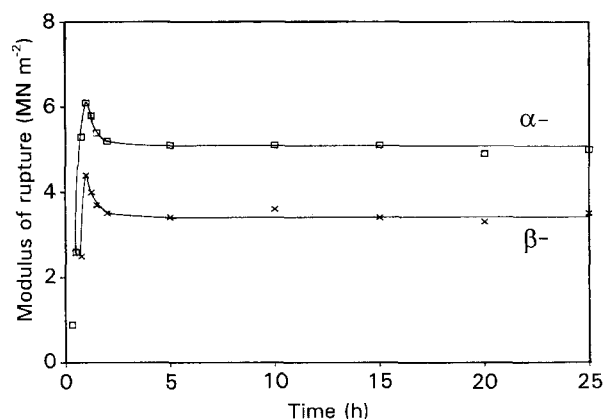


Figure 5 The development of “wet” strength as the hemihydrate sets.

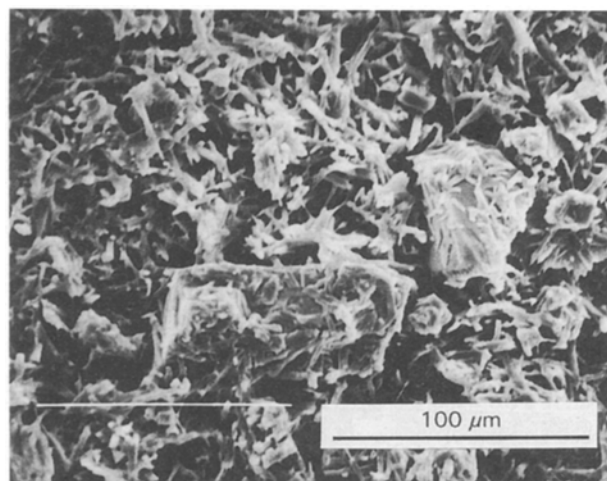


Figure 6 Scanning electron micrograph of the solid phases present in a partially reacted mixture of α -hemihydrate and water after 45 min (W/P ratio = 0.6).

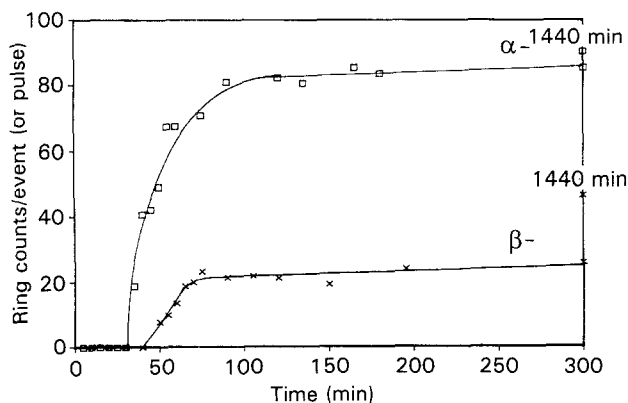


Figure 7 The acoustic transmittance (measured as ring counts/event) of setting hemihydrates (W/P ratio = 0.6).

Acoustic emission studies detected no signals during the setting process which indicates that surface microcracking, with a subsequent release of energy, was not responsible for the observed strength decrease in the second stage of strength development. It would therefore appear that internal pressure due to dihydrate crystallization is responsible. When acousto-ultrasonic testing was used to follow the microstructural development of the setting plasters, the ring counts per event or the average amplitude of events were measured as a function of time. These are both measures of the acoustic transmittance which, in turn, is a measure of the rigidity of the structure. The acoustic transmittance, measured as ring counts/events, of the setting plasters is shown in Fig. 7. No signal was obtained until a continuous solid structure is formed, which is earlier for the setting α -form. Both setting plasters gave an initial maximum transmittance after 90 min, indicating that the formation of the interlocking dihydrate crystal matrix was complete. However, the acoustic transmittance of the α -plaster was double that of the β -form, suggesting that the degree of intercrystalline bonding is far greater in the structure of the α -plaster. Both plasters also showed a significant increase in acoustic transmittance over the next 23 h. This gave complementary evidence for the theory that the increase in strength during the third stage of setting was due to the loss of lubricating water and the "cementing" of the structure by precipitated dihydrate from the remaining solution. This effect is more marked with the β -form because the initial degree of intercrystalline bonding is far less and therefore dihydrate precipitation between the sheaves of needles would result in a greater gain in intercrystalline bonding.

4.3. The relationship between the dihydrate crystal growth rates and the microstructure

Examination of the microstructure of the setting plasters, using a constant W/P ratio to ensure a constant porosity, showed that high strength and greater intercrystalline bonding was associated with a crystal habit of short, stubby dihydrate needles. This microstructure was typical of the set α -plaster, whilst set

β -plasters showed branching fibrous needles growing from nucleation sites.

The faster precipitation rate of the β -hemihydrate [7] resulted in faster crystal growth of a uniaxial nature. The result of this is a microstructure of lower strength.

The morphology of crystals grown from solution is known to depend on the rate of growth of the close packed faces [13]. The gypsum structure has calcium and oxygen ions most closely packed in the [001] direction [14], which is perpendicular to the direction of the layered lattice arrangement [15]. This is where double layers of CaSO_4 alternate with double layers of H_2O molecules. Because β -hemihydrate has a faster precipitation rate and therefore a faster crystal growth rate, it is energetically more favourable for growth to occur along the [001] direction, resulting in the observed uniaxial growth.

5. Conclusions

1. The setting, or development of strength, of gypsum plasters is a three-stage process:

(i) the first stage is the development of an interlocking matrix of dihydrate needles which is the result of the hydration reaction of hemihydrate;

(ii) the second stage is the relief of internal stress caused by the build-up of pressure as needles advance against each other. This stage is accompanied by a period of reduced strength;

(iii) the final stage involves the removal of water in excess of that required for the chemical reaction. The strength increased as the lubricating solution evaporated with the final structure containing a large amount of open porosity. Salts in solution precipitate out at this stage "cementing" the matrix together.

2. The α -hemihydrate "sets" faster than the β -form with higher initial and final set strengths.

3. The reaction of the α -plaster with water results in the dihydrate having a slower precipitation than that with the β -form/water reaction. The result is that the microstructure of the set α -plaster consists of relatively short stubby dihydrate needles with a greater degree of intercrystalline bonding and hence greater strength. The set β -plaster microstructure has longer, fibrous, branching sheaves of dihydrate needles with less intercrystalline bonding and therefore is of lower strength.

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