# Chapter 3
# Gypsum Products for Dental Casts

## 3.1 Introduction

Gypsum is a naturally occurring, white powdery mineral with the chemical name calcium sulphate dihydrate ($CaSQ_4 \cdot 2H_2O$). Gypsum products used in dentistry are based on calcium sulphate hemihydrate ($CaSO4_2)_2 \cdot H_2O$. Their main uses are for casts or models, dies and investments, the latter being considered in Chapter 5.

Many dental restorations and appliances are constructed outside the patient's mouth using models and dies which should be accurate replicas of the patient's hard and soft tissues.

The term *model* is normally used when referring to a replica of several teeth and their associated soft tissues or, alternatively, to an edentulous arch. The term *die* is normally used when referring to a replica of a single tooth.

The morphology of the hard and soft tissues is recorded in an impression and models and dies are prepared using materials which are initially fluid and can be poured into the impression, then harden to form a rigid replica.

Many materials have been used for producing models and dies but the most popular are the materials based on gypsum products.

The current ISO Standard for Dental Gypsum Products identifies five types of material as follows:

Type 1     Dental plaster, impression
Type 2     Dental plaster, model
Type 3     Dental stone, die, model
Type 4     Dental stone, die, high strength, low expansion
Type 5     Dental stone, die, high strength, high expansion

The Type 1 material will be discussed in Chapter 17 (Non-elastic Impression Materials).

## 3.2 Requirements of dental cast materials

The main requirements of model and die materials are dimensional accuracy and adequate mechanical properties. The accuracy of fit of any restoration or appliance constructed outside the mouth depends *inter alia* on the dimensional accuracy of the replica on which it is constructed. Thus, the dimensional changes which occur during and after the setting of these model materials should, ideally, be minimal in order to produce an accurate model or die. The final fit of the appliance may depend upon a balancing of small expansions or contractions which occur at different stages in its construction and it would be unwise to consider, in isolation, dimensional changes occurring with the model and die materials.

Although small dimensional changes during setting can often be tolerated and even compensated for, changes occurring during storage are a more serious problem. Hence, the dimensional stability after setting should be as good as possible.
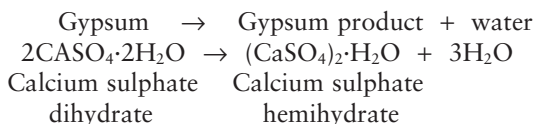
The material should, ideally, be fluid at the time it is poured into the impression so that fine detail can be recorded. A low contact angle between the model and impression materials would help to minimize the presence of surface voids on the set model by encouraging surface wetting.

The set material should be sufficiently strong to resist accidental fracture and hard enough to resist abrasion during the carving of a wax pattern.

The material should be compatible with all the other materials with which it comes into contact. For example, the set model should easily be removed from the impression without damage to its surface and fracture of teeth. It should give a good colour contrast with the various waxes which are often used to produce wax patterns.

## 3.3 Composition

Gypsum products used in dentistry are formed by driving off part of the water of crystallization from gypsum to form calcium sulphate hemihydrate.

$$Gypsum \rightarrow Gypsum\ product + water$$
$$2CASO_4 \cdot 2H_2O \rightarrow (CaSO_4)_2 \cdot H_2O + 3H_2O$$

Calcium sulphate     Calcium sulphate
    dihydrate           hemihydrate

Applications of gypsum products in dentistry involve the reverse of the above reaction. The hemihydrate is mixed with water and reacts to form the dihydrate.

$$(CsSO_4)_2 \cdot H_2O + 3H_2O \rightarrow 2CaSO_4 \cdot 2H_2O$$
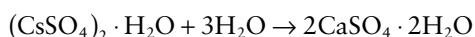
The various types of gypsum product used in dentistry are chemically identical, in that they consist of calcium sulphate hemihydrate, but they may differ in physical form depending upon the method used for their manufacture.

*Dental plaster (plaster of Paris):* Dental plaster is indistinguishable from the white plaster used in orthopaedics for stabilizing fractured limbs during bone healing. Plaster is produced by a process known as calcination. Gypsum is heated to a temperature of about 120°C in order to drive off part of the water of crystallization. This produces irregular, porous particles which are sometimes referred to as β-hemihydrate particles (Fig. 3.1a). Overheating the gypsum may cause further loss of water to form calcium sulphate anhydrite ($CaSO_4$), whilst underheating produces a significant concentration of residual dihydrate. The presence of both components has a marked influence upon the setting characteristics of the resultant plaster.

*Dental stone:* Dental stones may be produced by one of two methods. If gypsum is heated to about 125°C under steam pressure in an autoclave a more regular and less porous hemihydrate is formed (Fig. 3.1b). This is sometimes referred to as an α-hemihydrate.

Alternatively, gypsum may be boiled in a solution of a salt such as $CaCl_2$. This gives a material similar to that produced by autoclaving but with even less porosity. Manufacturers normally add small quantities of a dye to dental stones (see Fig. 3.2) in order that they may be differentiated from dental plaster, which is white.
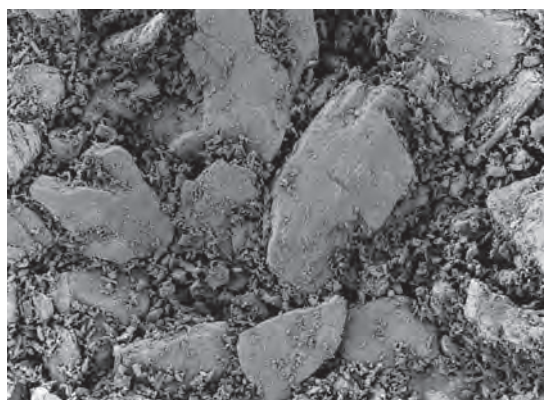


Fig. 3.1(a)    Particles of calcium sulphate β-hemihydrate (dental plaster) (×235).



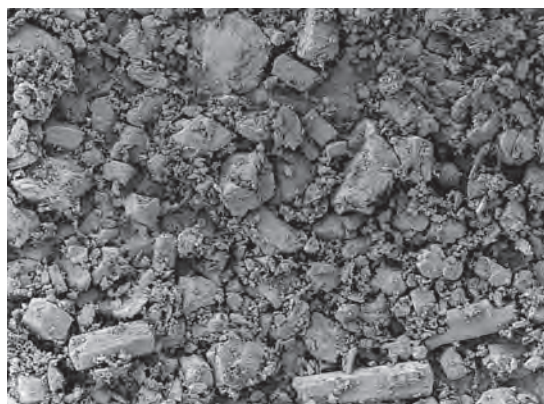Fig. 3.1(b)    Particles of calcium sulphate α-hemihydrate (dental stone) (×235).

## 3.4 Manipulation and setting characteristics

Plaster and stone powders are mixed with water to produce a workable mix. Hydration of the hemihydrate then occurs producing the gypsum model or die.

Table 3.1 gives an indication of the water/powder (W/P) ratio used for each material along with the theoretical ratio required to satisfy the chemical reaction which occurs. Although a ratio of only 0.186 is required to satisfy the reaction, such a mix would be too dry and unworkable. In the case of the more dense material, dental stone, a ratio of about 0.3 is required to produce a workable mix, whereas for the more porous plaster a higher W/P ratio of 0.55 is required. The excess water is absorbed by the porosities of the plaster

particles. Considerable quantities of air may be incorporated during mixing and this may lead to porosity within the set material. Air porosity may be reduced either by vibrating the mix of plaster or stone in order to bring air bubbles to the surface or by mixing the material mechanically under vacuum, or both.

For hand mixing a clean, scratch free rubber or plastic bowl having a top diameter of about 130 mm is normally recommended. The presence of gypsum residues in the mixing bowl can noticeably alter the working and setting characteristics of a fresh mix and so the need for cleanliness is emphasized. A stiff spatula with a round-edged blade of around 20–25 mm width and 100 mm length is used. The requisite amount of water is added to a moist bowl and the powder added slowly to the water over about 10 seconds. The mix is allowed to soak for about another 20



Fig. 3.2  Dental stone. This shows powdered dental stone which is a gypsum product commonly used in dentistry for making casts and models. Note the colour of the stone which in this case is pale yellow. This is to enable the user to distinguish it from dental plaster which although chemically similar is of a different physical nature and is normally white coloured. In use, the powder is mixed with water to form a paste which then hardens to form a hard mass.

Table 3.1  Water/powder ratios for gypsum model and die materials.

|  | Water (ml) | Powder (g) | W/P ratio (ml/g) |
| --- | --- | --- | --- |
| Plaster | 50–60 | 100 | 0.55 |
| Stone | 20–35 | 100 | 0.30 |
| Theoretical ratio | 18.6* | 100 | 0.186 |

* Sometimes referred to as gauging water.

seconds and then mixing/spatulation carried out for around 60 seconds using a circular stirring motion. After the material has been mixed and used, the mixing bowl should be thoroughly cleaned before the next mix is performed.

The fluidity of dental gypsum products is normally measured by one of two methods outlined in the ISO Standard. For types 1 and 2 materials a *slump* test is recommended. Here, a known volume of mixed material is allowed to *slump* onto a glass plate at a time indicated by the manufacturer as the pouring time (2–3 minutes for most materials). The fluidity is defined as the average of the major and minor diameters of the slumped material.

The fluidity of types 3, 4 and 5 materials is determined using a core penetration test. The depth of penetration of a core falling under a load for 15 seconds into a known quantity of material is measured 3 minutes after starting to mix powder and water.

The setting process begins rapidly after mixing the powder and water. The first stage in the process is that the water becomes saturated with hemihydrate, which has a solubility of around 0.8% at room temperature. The dissolved hemihydrate is then rapidly converted to dihydrate which has a much lower solubility of around 0.2%. Since the solubility limit of the dihydrate is immediately exceeded it begins to crystallize out of solution. The process continues until most of the hemihydrate is converted to dihydrate.

The crystals of dihydrate are spherulitic in nature and grow from specific sites called nuclei of crystallization. These may be small particles of impurity, such as unconverted gypsum crystals, within the hemihydrate powder. If a thin mix of material is used, containing more water than that indicated in Table 3.1, the formation of the supersaturated solution of dihydrate which is a precursor to crystallization is delayed and the centres of nucleation are more widely dispersed by the dilution effect. The set plaster is therefore less dense with greater spaces between crystals leading to a significant reduction in strength.

The material should be used as soon as possible after mixing since its viscosity increases to the stage where the material is unworkable within a few minutes. Two stages can be identified during setting. The first is the time at which the material develops the properties of a weak solid and will not flow readily. At this time, often referred to as

the initial setting time, it is possible to carve away excess material with a knife. The materials continue to develop strength for some time after initial setting and eventually reach a stage when the models or dies are strong and hard enough to be worked upon. The time taken to reach this stage is referred to as the final setting time, although this term is misleading since it implies that the material has reached its ultimate strength. This may not be reached until several hours after mixing.

The setting characteristics of gypsum products can be affected not only by the presence of unconverted dihydrate but also by the presence of anhydrite, the age of the material and the storage conditions experienced by the material prior to use. Small quantities of unconverted dihydrate act as centres of nucleation as mentioned earlier. Anhydrite reacts very rapidly with water producing a marked acceleration in setting. Freshly produced plaster may contain significant quantities of anhydrite (Section 3.3) and this may accelerate setting to the extent that manipulation becomes difficult. To overcome this problem plaster is often allowed to mature before use, the anhydrite absorbs moisture and is converted to the less reactive hemihydrate. If the plaster is allowed to mature for too long in a humid environment the hemihydrate crystals become coated with a layer of dihydrate and the reactivity is markedly reduced.

The setting characteristics of gypsum products have traditionally been measured in terms of their ability to resist penetration by needles, such as those shown in Fig. 3.3. The heavier needle has a smaller tip diameter than the lighter one and hence applies a considerably greater pressure to the surface of the material under test. The initial setting time is defined as the time taken for the material to develop sufficient strength such that it is able to support the lighter of the needles. The time at which the material is able to support the heavier needle has doubtful practical significance since it indicates a time somewhere between the initial and final setting times and is not indicative of the fact that the model or die is hard enough to be used.

The ISO specification for dental gypsum products requires the use of a Vicat needle for judging setting time. This system has a built-in dial gauge allowing depth of penetration to be measured. Also the load can be varied in order to satisfy the



Fig. 3.3  Indentors used to assess setting characteristics of gypsum products. Sometimes referred to as Gilmore needles. Ability of support needle (b) indicates the initial set. Ability to support needle (a) indicates final set.
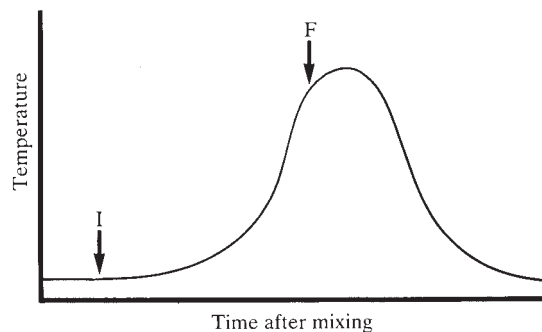


Fig. 3.4  Temperature–time profile for a gypsum material during setting. Points I and F correspond to the initial set and final set points indicated by indentors (Fig. 3.3).

requirements of several standard tests. The setting material is indented by a needle of 1 mm diameter under a load of 300 g. The setting time in this test is defined rather arbitrarily as the time when the needle is no longer able to penetrate to a depth of 2 mm into the material. The setting time measured using this method is normally less than 30 minutes, however a longer time is required before the material has matured sufficiently to allow any further work to be performed on the cast without damaging the surface.

The setting reaction is exothermic, the maximum temperature being reached during the stage when final hardening occurs (Fig. 3.4). It is interesting

to note that the temperature rise is still negligible at the time of the initial set. The magnitude of the temperature rise depends on the bulk of material used and can be as great as 30°C at the centre of a mass of setting material. This temperature may be maintained for several minutes due to the thermal insulating characteristics of the materials. This marked rise in temperature can be used to good effect when flasking dentures since it softens the wax of the trial denture and enables it to be easily removed from the mould.

Another physical change which accompanies setting is a small expansion caused by the outward thrust of growing crystals as shown in Fig. 3.5. The maximum rate of expansion occurs at the time when the temperature is increasing most rapidly. The expansion is, in fact, only apparent since the set material contains a considerable volume of porosity. If the material is placed in water at the initial set stage, considerably more expansion occurs during setting. This increased expansion is called *hygroscopic expansion* and is sometimes used to increase the setting expansion of gypsum-bonded investment materials (Chapter 5).

The setting expansion is measured using a special trough with a moveable end-plate which pushes against an extensometer. Mixed material is poured into the trough and as it solidifies and expands the extensometer is displaced, giving a value of linear expansion. The maximum expansion values are as great as 0.15% for type 1 and 4 materials and 0.30% for type 2 and 5 materials. Type 3 materials have a maximum expansion of 0.20%. Some individual products have much lower values of expansion (see Table 3.2).

*Control of setting time:* Factors which control the setting times of gypsum products can be divided into those controlled by manufacturers and those controlled by the operator.

The manufacturer can control the concentration of nucleating agents in the hemihydrate powder. A higher concentration of nucleating agent, produced by ageing or from unconverted calcium sulphate dihydrate, results in more rapid crystal-
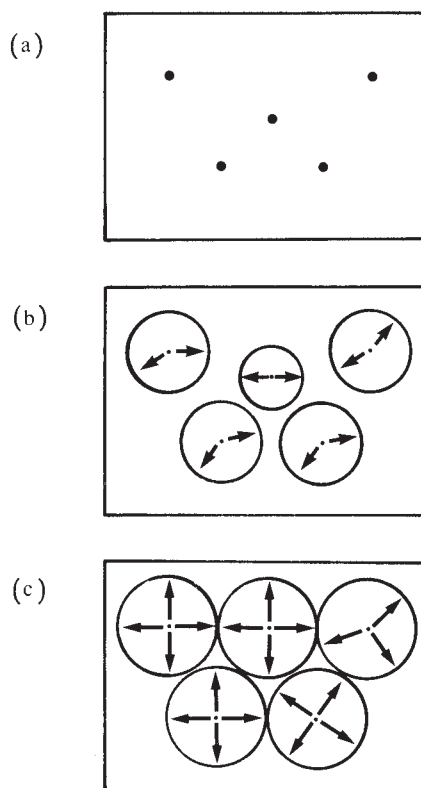


Fig. 3.5   Diagram showing growth of spherulitic gypsum crystals, indicating (a) the nuclei from which crystals grow, (b) spherulitic growth and (c) the outward thrust as spherulites make contact.

Table 3.2   Properties of dental gypsum products (typical values).

| Property | Type 1 | Type 2 | Type 3 | Type 4 | Type 5 |
|---|---|---|---|---|---|
| Initial setting time (min) | – | 5–10 | 5–20 | 5–20 | 5–20 |
| Setting time (min) | 4 | 20 | 20 | 20 | 20 |
| Setting expansion (%) | 0–0.15 | 0–0.30 | 0–0.20 | 0–0.15 | 0.16–0.3 |
| Compressive strength 1 h (MPa) | 6 | 12 | 25 | 40 | 40 |
| Compressive strength 24 h (MPa) | – | 24 | 70 | 75 | 75 |
| Flexural strength 24 h (MPa) | 1 | 1 | 15 | 20 | 20 |
| Detail reproduction (μm) | 75 | 75 | 50 | 50 | 50 |

lization. Also, the manufacturers may add chemical accelerators or retarders to dental stones. Potassium sulphate is a commonly used accelerator which is thought to act by increasing the solubility of the hemihydrate. Borax is the most widely used retarder, although the mechanism by which it works is not clear.

Factors under the control of the operator are temperature, W/P ratio and mixing time. Surprisingly, temperature variation has little effect on the setting times of gypsum products. This is due to the fact that the setting involves a dissolution of one sparingly soluble salt followed by crystallization of another. Increasing the temperature accelerates the solution process but retards the crystallization. Thus the two effects tend to cancel out. Increasing the W/P ratio retards setting by decreasing the concentration of crystallization nuclei. Increasing mixing time has the opposite effect. This accelerates setting by breaking up dihydrate crystals during the early stages of setting, thus producing more nuclei on which crystallization can be initiated. These effects are shown in Fig. 3.6.

*Control of setting expansion:* In order to produce an accurate model or die it is necessary to maintain the setting expansion at as low a value as possible. Accelerators or retarders which are added by manufacturers to dental stones in order to control the setting time also have the effect of reducing the setting expansion and are sometimes referred to as *antiexpansion agents*. The final

values of expansion observed for typical materials are given in Table 3.2. The very low value of expansion for some stones may be considered negligible in terms of its effect on the accuracy of restorations or appliances which are to be constructed.

Alterations in W/P ratio and mixing time have only a minimal effect on setting expansion.

## 3.5  Properties of the set material

The strength of gypsum depends, primarily, on the porosity of the set material and the time for which the material is allowed to dry out after setting.

The porosity, and hence the strength, is proportional to the W/P ratio as shown in Fig. 3.7.

Since stone is always mixed at a lower W/P ratio than plaster it is less porous and consequently much stronger and harder.

Although a gypsum model or die may appear completely set within a relatively short period its strength increases significantly if it is allowed to stand for a few hours. The increase in strength is a function of the loss of excess water by evaporation. It is thought that evaporation of water causes a precipitation of any dissolved dihydrate and that this effectively cements together the crystals of gypsum formed during setting.

Despite precautions which may be taken to ensure optimum mechanical properties, gypsum is a very brittle material. The very low value of flexural strength of plaster shown in Table 3.2 is indicative of how fragile this material is. Stone is
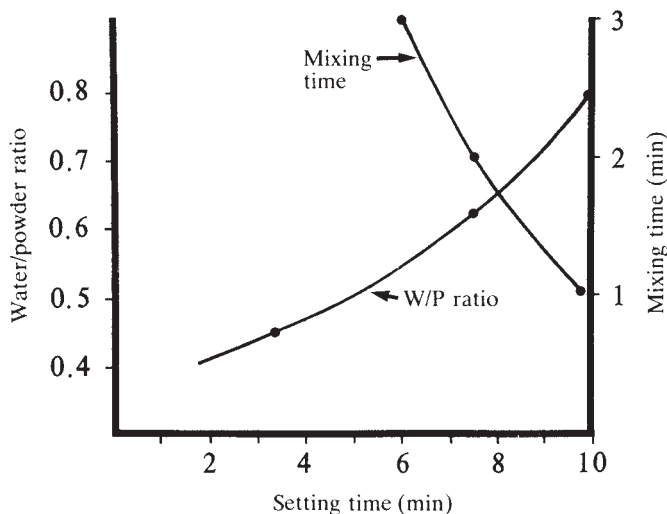


Fig. 3.6   The effect of water/powder ratio and mixing time on setting time for a typical dental plaster.
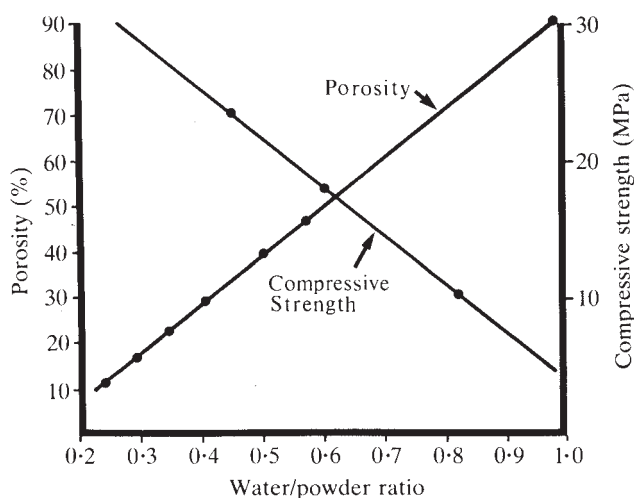
Fig. 3.7 The effect of water/powder ratio on the porosity and compressive strength of gypsum products.

less fragile but must be treated with care if fracture is to be avoided. It is relatively rigid but has a poor impact strength and is likely to fracture if dropped. Attempts to improve the mechanical properties have involved the impregnation by a polymer such as acrylic resin and the use of wetting agents which enable the materials to be used at a lower W/P ratio.

The dimensional stability of gypsum is good. Following setting, further changes in dimensions are immeasurable and the materials are sufficiently rigid to resist deformations when work is being carried out upon them.

The ability of dental gypsum products to reproduce surface details of hard or soft tissues either directly or from impressions is central to their suitability as model and die materials. This ability is judged by measuring the extent to which accurately machined lines in a block of stainless steel can be reproduced in a sample of the material. Types 1 and 2 materials can reproduce a groove 75 μm wide whilst types 3, 4 and 5 are able to reproduce grooves of only 50 μm width. Hence, types 3, 4, and 5 stones are capable of recording greater fine detail than type 2 (plaster) material.

Set plaster is slightly soluble in water. Solubility increases with the temperature of the water and if hot water is poured over the surface of a plaster cast, as happens during the boiling out of a denture mould, a portion of the surface layer becomes dissolved leaving the surface roughened. Frequent washing of the surface with hot water should therefore be avoided.

Table 3.2 gives comparative values of properties for the different types of dental gypsum products.

## 3.6 Applications

When strength, hardness and accuracy are required dental stones are normally used in preference to dental plaster. The stone materials are less likely to be damaged during the laying down and carving of a wax pattern and give optimal dimensional accuracy. Thus, these materials are used when any work is to be carried out on the model or die as would be the case when constructing a denture on a model or a cast alloy crown on a die.

When mechanical properties and accuracy are not of primary importance the cheaper dental plaster is used. Thus, plaster is often used for mounting stone models onto articulators and sometimes for preparing study models.

## 3.7 Advantages and disadvantages

Gypsum model and die materials have the advantages of being inexpensive and easy to use. The accuracy and dimensional stability are good and they are able to reproduce fine detail from the impression, providing precautions are taken to prevent blow holes.

The mechanical properties are not ideal and the brittle nature of gypsum occasionally leads to fracture – particularly through the teeth, which form the weakest part of any model.

Problems occasionally arise when gypsum model and die materials are used in conjunction with alginate impression. The surface of the model may remain relatively soft due to an apparent retarding effect which hydrocolloids have on the setting of gypsum products. It is not certain whether the retarding effect is due to borax in the hydrocolloid or to the absorption of hydrocolloid onto the gypsum crystals which act as nuclei of crystallization. Despite these observations it cannot be said that gypsum products are incompatible with alginate impression materials since problems arise very infrequently.

Alternative materials for the production of models and dies exist but are hardly ever used. These include various resins, cements and dental amalgam. The alternatives may be stronger but are generally less stable, difficult to use and more expensive. The surface of a gypsum die can be hardened by electroplating the impression prior to constructing the die. The thin layer of metal, copper for impression compound and silver for some elastomers, is transferred to the surface of the die on separation from the impression.

Another treatment which has been suggested for improving the durability of gypsum is to partly saturate the set material in a polymerizable monomer such as methylmethacrylate or styrene. Polymerisation of the monomer produces a polymer phase which occupies many of the porosities in the set gypsum and increases its strength and toughness. Despite these apparent advantages these techniques are rarely used in practice.

## 3.8 Suggested further reading

Combe, E.C. & Smith, D.C. (1964) Some properties of gypsum plasters. *Br. Dent. J.* **117**, 237.

Earnshaw, R. & Marks, B.J. (1964) The measurement of the setting time of gypsum products. *Aust. Dent. J.* **9**, 17.

Fairhurst, C.W. (1960) Compressive properties of dental gypsum. *J. Dent. Res.* **39**, 812.