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Investigation of the setting of polyamide fibre/latex-filled plaster composites

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Abstract

We have investigated the setting of binary blends (latex-filled plaster and polyamide fibre-reinforced plaster materials) and ternary blends (polyamide fibre-reinforced latex-filled plaster materials). The influences of the latex (nature and concentration) and the fibres (concentration, length and diameter) were analysed in terms of the setting time, the total swelling and the hydration of the plaster. The association of hydrophilic polyamide fibres with plaster disturbs the hydration, and the setting time of the plaster/latex binary blends depends strongly on the nature of the polymer. The choice of the proper latex to be associated with the plaster was made looking upon its influences on the setting time and the mechanical properties of the blend. The ternary blends were characterised by a drastic increase of the setting time correlated with a reduction of the total swelling.

Keywords: Fibres; Plaster setting; Composites; Microstructure-final; Structural applications

1. Introduction

A great deal of research has been focused on the setting of plaster and the mechanical behaviour of the resulting materials.[1–10] It comes out that the poor mechanical properties of plaster are ascribed to the high porosity and the low cohesion between the grains as the integrity essentially relies on the interlocking of the grains. Attempts for increasing the mechanical properties of plaster include microstructural control by means of gypsum grains seeding,[11,12] prestressing during the setting[12] or reinforcing using synthetic fibres (glass, polyamide) or natural fibres (sisal, waste paper).[1–3,9,10] Another way for increasing the mechanical properties of plaster while retarding moisture penetration may consist in the addition of polymer latexes.[13] Since their commercial introduction in the early 1950s, epoxy resins in particular, and polymer latexes in general, have been associated with mortars and concretes in the aim to increase the Young's modulus, the strength and the fracture toughness. But the hydration could be delayed by the adsorption of the polymer particles on the surface of the cement grains, which results in a limitation of the cement dissolution and a reduction of the germination sites. The consequence is an increase of the setting time with the concentration of latex.[14–17]

The purpose of the study presented in this paper was to examine the effects of different latexes and a hydrophilic synthetic fibre on the setting of plaster. The setting was assessed by two methods: the dimensional variation of standard specimens monitored by mean of a home-made contact-free optical measurement set and hydration measurements of the plaster at different dates.

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Table 1
Characteristics of the latexes

	PAV22P	PAV30	PA050	DEC27	DS931
Chemical nature	(Powder) vinyl acetate/vinyl versatate copolymer dispersable in water	(Powder) vinyl acetate/vinyl versatate copolymer (higher amount of versatate) dispersable in water	(Powder) vinyl acetate homopolymer dispersable in water	Anionic aqueous dispersion of acrylic/esters copolymer	Anionic aqueous dispersion of an acrylic/styrene copolymer
Aspect	White powder dispersible in water	White powder dispersible in water	White powder dispersible in water	Milky liquid	Milky liquid
Solid phases (s.p.) or dry extracts (d.e.) (wt.%)	(s.p.) 99 ± 1	(s.p.) 99 ± 1	(s.p.) 99 ± 1	(d.e.) 48 ± 1	(d.e.) 50 ± 1
Diameter of particles (μm)	1–5	1–5	1–5	0.1	0.12
Minimum temperature for film formation (°C)	+5	+5	0	+3	+20

2. Experimental

2.1. Materials

A standard commercial plaster (Lutèce 75 from BPB Placo Lambert, Paris), made of 50–70% of a β type hemihydrate (i.e. 50–30% of $CaSO_4$), was used for this study. The latexes were commercial products supplied by Rhodia, Centre of Aubervilliers in France, in form of powders or aqueous solutions of polymers in suspension. They were tailored to raise the adhesion, handiness and waterproofness properties of plaster or cement mortars. The powders were vinyl acetate homopolymer (PA050) or copolymers (PAV22P and PAV30), while the suspensions were polymeric dispersions in water of a styrene acrylate copolymer (DS931) or an acrylate ester copolymer (DEC27). The main characteristics of these latexes are given in Table 1.

For the elaboration of the plaster/latex binary blends, the desired concentration of the latex (1, 2, 3, 4, 5, 7, 8 or 10 wt.%) was first dispersed in water and then the plaster powder was poured and mixed to obtain the binary blend (mixing mass ratio water/dry materials is 0.68). In the case of the polymer dispersions DS931 and DEC27, the water used for the dispersion was taken into account for adjusting the mixing water.

Polyamide (PA) fibres supplied by Rhodia were used in different morphologies (4, 6, 9 and 18 mm long, with a diameter of 10 and 19 μm; Young's modulus of 2 GPa, tensile strength of 500 MPa and ultimate strain of 200%). For the elaboration of the plaster/fibre binary blends, the desired concentration of fibres (1, 2, 3, 4 or 6 wt.%) was first dispersed into water before adding the plaster. As the PA fibres are hydrophilic, the bundles dissociate easily into individual fibres when mixed with water.

For the elaboration of the ternary blends, the desired concentration (1, 2, 4 or 6 wt.%) of polyamide fibres 6 mm long with a diameter of 19 μm was added to the latex/water mix (with a latex concentration of 2, 5 or 8 wt.%) before the plaster powder was poured.

All the batches of composite materials were elaborated according the same protocol as for the neat plaster. The mixing mass ratio used was 0.68, and in order to keep the same extent of hydration of plaster, the fibre weight had been subtracted from the plaster weight. Standard specimens with dimensions 160 mm × 40 mm × 40 mm and 80 mm × 40 mm × 40 mm were fabricated, exposed for 1 day in air at room temperature and stored for 7 days in an oven at 40 °C for the plaster drying.

2.2. Methods

2.2.1. Measurement of the dimensional variations

The dimensional variations of the specimens during the setting were monitored by using a new contact-free measurement set, developed in our Institute. The equipment consists in a high precision optical profilometer and makes use of a laser and a triangulation method.[18]

2.2.2. Temperature change and conductivity measurements

An ultra flat Pt 100 probe (1 mm thick with area 6 mm^2) was used to monitor the temperature change during the setting. This probe was attached to the outer side of the mould wall, in contact with the heat flow from the plaster through a 2 mm hole. Two flat steel plates immersed in the mixture were used to monitor the conductivity during the setting.

2.2.3. Evaluation of the hydration of the plaster

The influence of the additives on the hydration of the plaster has been investigated by comparing the hydration of the plaster in the blends to the one of the neat plaster, at different dates. The hydration of plaster can be determined by quantifying the dihydrate (gypsum) $CaSO_4$, $2H_2O$. This quantification was made by using two techniques: infrared spectroscopy (IR) which measures the area of the peaks at 1621 and 1685 cm^{-1} (which correspond to the vibration of the water molecules in the gypsum) and thermogravimetric analysis (TGA) which determines the mass loss at 150 °C associated with the decomposition of the gypsum.

The hydration of the neat plaster and of the binary blends, containing 4 wt.% of polyamide fibres and 5 wt.% of latexes PAV30, PA050 or DEC27, has been stopped at regular points of 30, 60 and 90 min after the end of the mixing, by rinsing repeatedly in absolute ethanol and acetone. Thus, the specimens have been dried in an oven at 40 °C for 48 h, crushed and filtered using a 200 μm mesh sieve, in order to eliminate the synthetic fibres. For the infrared spectroscopy measurements, the powder has been diluted into KBr (5 wt.% of powder).

3. Results and discussion

3.1. Neat plaster

Plaster setting, i.e. the transformation of the hemihydrate (the plaster powder $CaSO_4$, $\frac{1}{2}H_2O$) in an aqueous solution into gypsum (set plaster $CaSO_4$, $2H_2O$), is an hydration process that may be sketched in two stages: dissolution of the hemihydrate, germination and growth of the gypsum. During and after hydration, plaster-based pastes are subject to different volume changes as a consequence of chemical and physical phenomena related to the hydration of the hemihydrate.[11,19–22] In previous works, it was evidenced that the influence of additives on the setting of plaster could be assessed through calorimetric or dimensional variation measurements.[9,14] Herein, conductivity measurements are correlated to calorimetric and dimensional measurements to investigate the setting characteristics of plaster composites. Fig. 1 shows the evolutions of the temperature and the conductivity, along with the shrinkage–swelling behaviour of the Lutèce 75 type plaster as a function of time. In this figure, it appears that the dimensional variation levels off by a time, which corresponds to the end of the setting, t_s. At the same time, the temperature reaches a maximum value, and we note an inflexion on the conductivity versus time curve. Thus, the setting time can be indiscriminately determined from one of these functions.

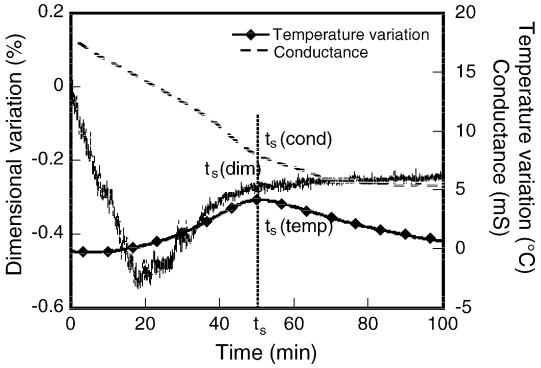

Fig. 1. Evaluation of the setting time of a neat plaster through a correlation of conductivity and calorimetric measurements with dimensional variations.

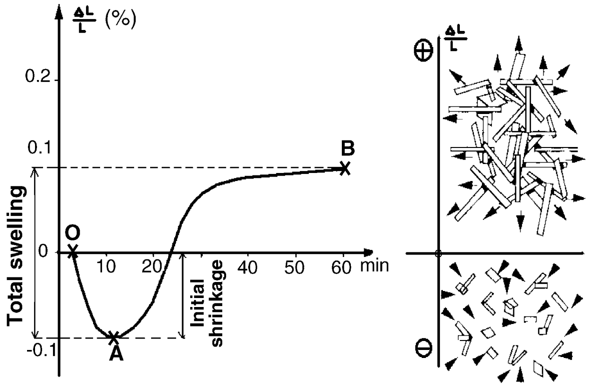

Fig. 2. Shrinkage–swelling diagram and phenomenological illustration of the shrinking and swelling stages.[11]

Interesting information can be obtained from the dimensional variation of the blend with time, as it is related to the dissolution of the plaster and the germination and growth of the gypsum crystals. In the typical shrinkage–swelling curve of plaster depicted in Fig. 2, domain OA is associated with a shrinkage as the volume of the mixture (hemihydrate and water) is smaller than the sum of the volumes of the hemihydrate and the added water. Shrinkage ends at point A where the plaster setting begins. At point A, the increased cohesion relatively to the preceding stage is due to Van der Walls forces and hydrogen bonds with water molecules within the micropores. A noticeable swelling stage then follows (AB domain), which is associated with the mutual repulsion of the gypsum grains now in close contact and still growing. At this stage, crystallized links form due to the effect of valence forces and a continuous solid structure develops.

The setting of the Lutèce 75 type plaster depicted in Fig. 1 is characterised by a pronounced shrinkage followed by a swelling not enough important to compensate for the shrinkage. This neat plaster sets in about 47 min; thus, we can consider for the determination of the hydration that the plaster is totaly hydrated after 90 min.

3.2. Plaster/fibre binary blends

Fig. 3a and b show the evolution of the setting time and the total swelling, respectively, as a function of the PA fibres concentration. The setting time decreases as the PA fibres length or concentration is raised (Fig. 3a), whereas we had noted no influence of the fibres diameter. This behaviour of the blends reveals a disturbance of the plaster hydration due to the PA fibres which can absorb some water and calcium ions during the mixing and the setting stages, and later on drop them. The disturbance of the plaster hydration by the PA fibres is corroborated by the comparison of the infrared spectra or the thermogravimetric diagrams of the neat plaster and of the

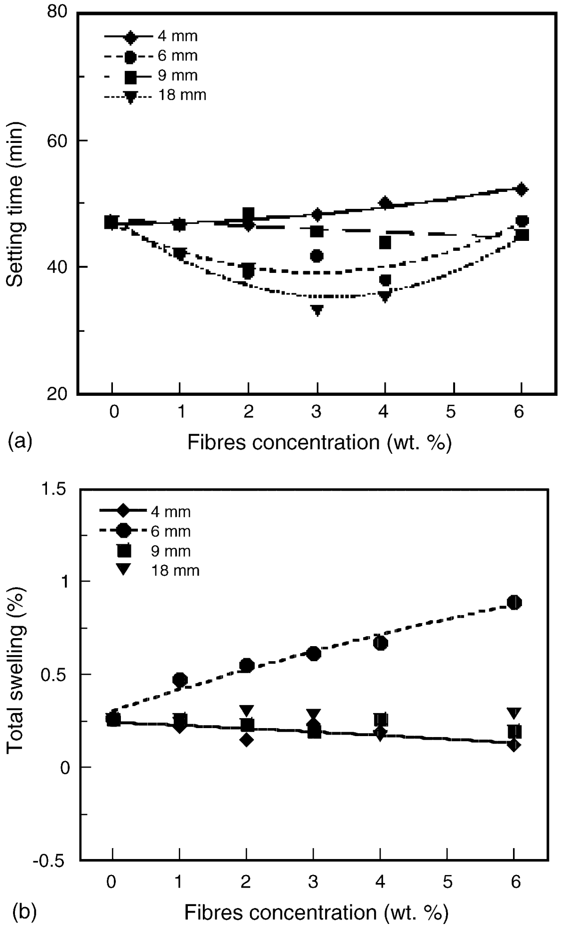

Fig. 3. Influences of the fibre concentration and length on the setting time (a) and the total swelling (b) of the plaster/fibres binary blends.

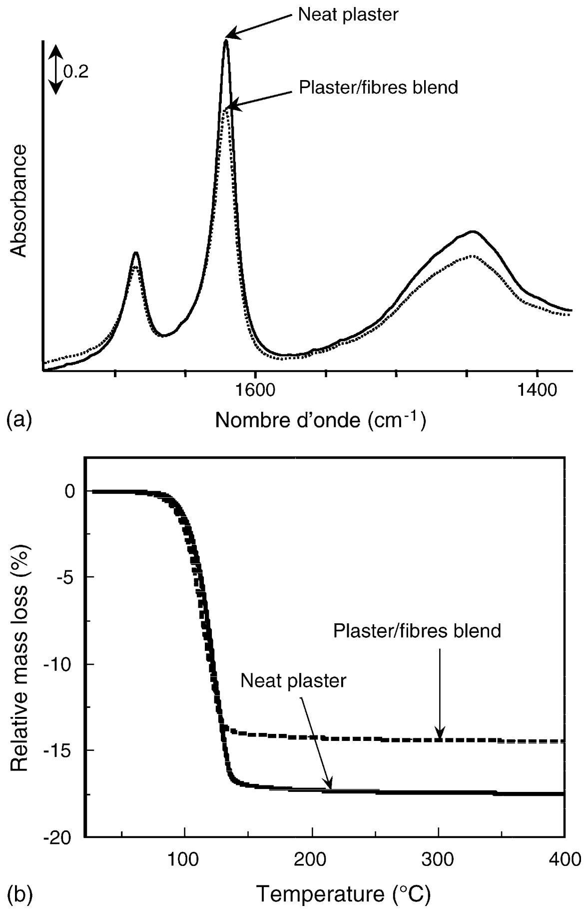

Fig. 4. Hydration degree of the neat plaster and a plaster/fibre blend determined after 90 min by using (a) the infrared spectra and (b) the thermogravimetric diagrams.

plaster/fibres blends at the different points (Fig. 4a and b). A relatively important delay of the plaster hydration is noted up to 60 min as the polyamide fibres absorb some water and calcium ions, and then the hydration degree strongly increases probably because the fibres drop the absorbed components. However, as the neat plaster is considered fully hydrated after 90 min, the hydration of the matrix in the plaster/fibres binary blends is about 20% lower than the potential value (Fig. 4b).

The evolution of the total swelling with the fibre content (Fig. 3b) shows a continuous downward trend for all the blends, which can be explained by a decrease of the amount of calcium sulphate dehydrate formed as the fibres concentration is increased. But with the 6 mm long fibres, a swelling of the blends is noted, which may be explained by the important porosity that develops because these fibres are uneasy to disperse in water, as they had been overdried.

3.3. Plaster/latex binary blends

Fig. 5 shows the dimensional variations during the setting of the neat plaster and of blends containing 5 wt.% of each type of latex. In comparison with the neat plaster, we note that the addition of the DS931-type latex, which includes a water-repellent component, results in an important initial shrinkage followed by a non noticeable swelling, and the setting is strongly delayed. Thus, the setting time increases

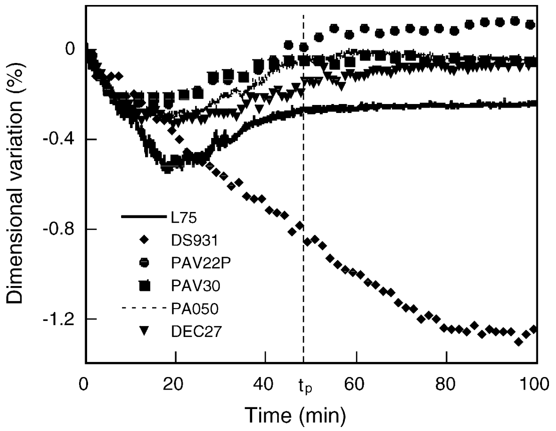

Fig. 5. Shrinkage–swelling behaviour during the setting of the plaster/latex blends.

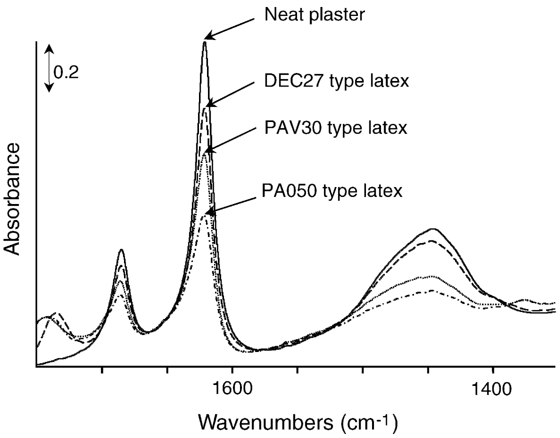

Fig. 6. Comparison of the infrared spectra of the neat plaster and of plaster/latex binary blends, after 90 min.

considerably with the concentration of latex: it reaches 120 min for 6 wt.% of latex. According to these results, the DS931-type latex seems not to promote a good hydration of plaster, and consequently might not be associated with the plaster.

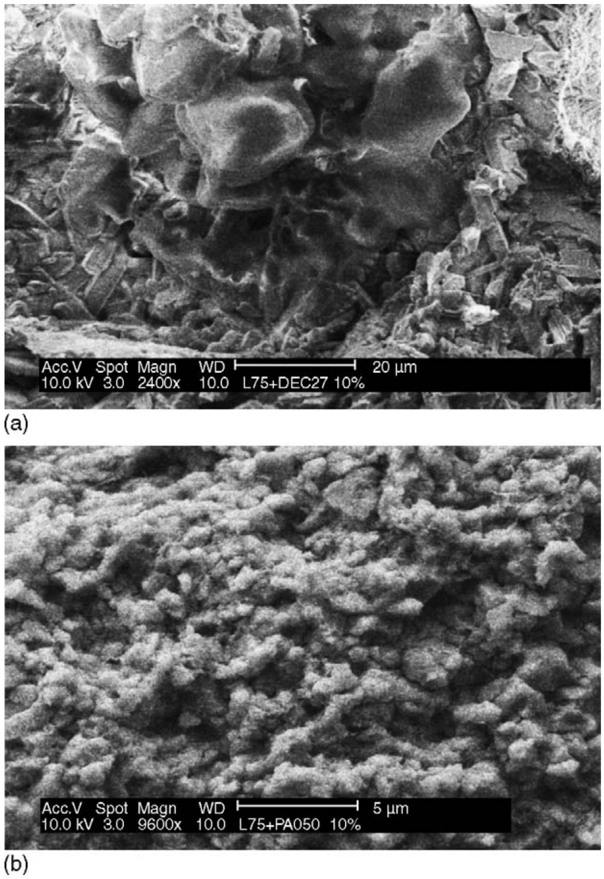

Fig. 7. Scanning electron micrographs showing a continuous amorphous film covering the gypsum crystals: 10 wt.% of (a) DEC27 and (b) PA050 latexes.

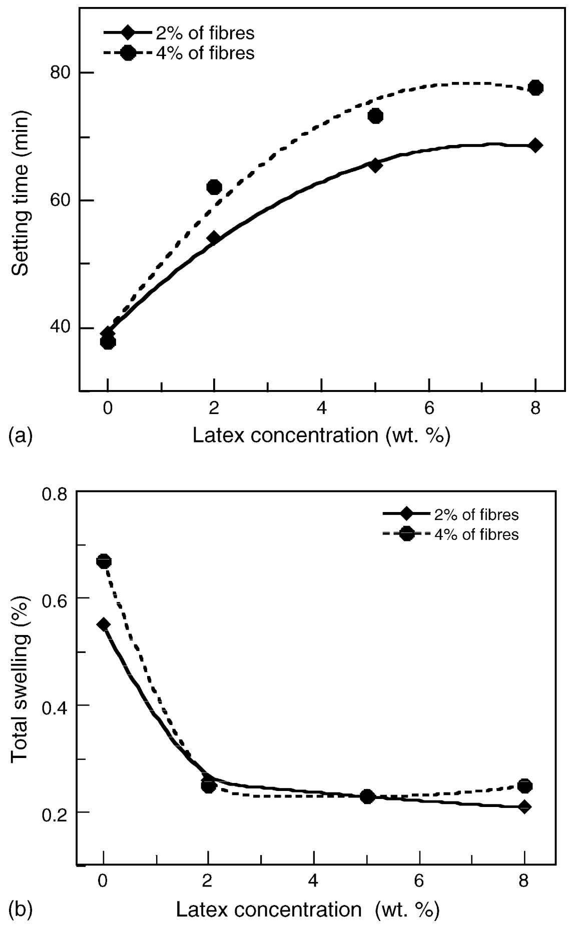

Fig. 8. Influences of the fibre and the PAV30-type latex concentrations on the setting time (a) and the total swelling (b) of the ternary blends.

The powdered latexes PAV22P, PAV30 and PA050 do not delay the setting of the blends (i), reduce the initial shrinkage of the neat plaster (ii), but do not affect the swelling (iii). For the blends containing the DEC27-type latex, the setting is only slightly delayed, the dimensional variations are the same as those of the others blends. The setting time and the dimensional variations of these binary blends are not dependent on the latex concentration.

The point (ii) calls for the question whether all the hemihydrate dissolves when latex is associated with the plaster; this seems to be the case according to the point (iii). In order to elucidate this question, investigations have been conducted on the hydration of the matrix. The comparison of the infrared spectra of the neat plaster and of plaster/latex binary blends after 90 min is shown in Fig. 6 for different latexes. It appears that the addition of a latex to the plaster results in a decrease of the hydration, as the quantity of dihydrate formed is reduced, according to point (ii). The polymer particles adsorbed on the surface of the plaster grains either delay the dissolution of the semihydrate (that is the case for the DEC27-type latex which shows the highest hydration after 90 min), or hinder the hydration of the plaster grains (that the case for the PAV30 and PA050 types of latex).[23] This is exemplified in Fig. 7a that shows gypsum crystals totally masked with a continuous amorphous layer of the DEC27 type latex, and in Fig. 7b in which the PA050 latex particles cover the hemihydrate grains.

3.4. Plaster/fibre/latex ternary blends

Conversely to the plaster/PAV30-type latex binary blends, the setting time of the ternary materials strongly increases with the concentration of the latex, and in a minor part with the amount of fibres (Fig. 8a). This trend can be explained by the fact that the polyamide fibres, which are able to absorb some water and calcium ions, can induce a local dehydration in their vicinity, which causes a more important adsorption of the polymer particles on the plaster grains and results in an increase of the setting time of the blends.

The latex particles act to hinder the hydration of some plaster grains and thus reduce the quantity of dihydrate formed. Consequently, the total swelling of the ternary blends decreases drastically as the latex concentration is increased up to 2 wt.%, and then levels off for higher amounts of the polymer (Fig. 8b).

4. Conclusions

The setting of plaster associated with polyamide fibres and/or polymer latexes has been investigated. Polyamide fibres disturb the hydration of the plaster as they absorb some water and calcium ions during the mixing and the beginning of the setting, and drop these components later during the setting. The setting time of plaster/latex binary blends is strongly dependent on the nature of the polymer: a latex containing a water-repellent component hinders the hydration of plaster. The other latexes also affect the dissolution of the hemihydrate by adsorption on the surface of the plaster grains; thereby, they hinder the hydration of some hemihydrate grains. The association of polyamide fibres and a latex with plaster results in a drastic increase of the setting time correlated with a reduction of the total swelling. The mechanisms invoked are a local dehydration induced by the polyamide fibres and an important adsorption of the polymer particles on the plaster grains.

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