

Microstructure characterization of polyamide fibre/latex-filled plaster composites

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Abstract

We have investigated the microstructure of polyamide fibre/plaster and latex-filled plaster binary blends, and fibre/latex-filled plaster ternary blends. The influences of the latex (nature and concentration) and the fibres (concentration, length) were analysed in terms of the gypsum crystals morphology, the distribution of the polymer phase and the porosity of the materials. Addition of polyamide fibres and/or polymer latexes to plaster results in a coarser crystallisation, and disturbs the hydration of plaster; the porosity raises with the amount of fibres but decreases with the concentration of latex. It is shown that the presence of latex may noticeably modify the porous network of the plaster. These results are correlated to the setting of the materials.

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1. Introduction

Plaster is a widely used building material all around the world, because of its availability, relative low cost and easiness to use. But some major drawbacks restrict the use of plaster, among which the low impact resistance, the pronounced brittleness and water-related degradation sensitivity. In order to reduce its brittleness, plaster is associated with natural fibres (sisal, waste paper) or synthetic ones (glass, polyamide).^{1–4} Another mean of reinforcing plaster may consist in the use of polymer latexes^{5,6} which were demonstrated to induce noticeable increases of the Young's modulus, strength and toughness^{7–11} when mixed with mortar or concrete. The reinforcement mechanisms invoked include a strengthening of the matrix and an improved load transfer upon drying as the polymer has partially filled up the pores.^{7–14} For the former mechanism to be efficient, a minimum amount of latex is required for the formation of a continuous film within the blend.¹⁴

In a previous study,¹⁵ we had investigated the setting of polyamide fibre/plaster and polymer latex/plaster binary blends and plaster/latex/fibres ternary blends. The following results were outlined:

- the presence of the polyamide fibres does not result in an increase of the setting time, in spite of the fact that the hydration degree of the plaster matrix is lowered in comparison to the neat plaster. A plausible explanation is that the fibres disturb the hydration of plaster by first absorbing some water and calcium ions during the mixing and the beginning of the setting, and later on dropping these matters during the setting;
- the influence of the latex on the setting of the plaster depends on the nature of the polymer: the DS931-type latex, which contains a water-repellent component, strongly delays the setting of the plaster, while the other types of latex do not increase the setting time or only lightly (DEC27-type latex). However, at different dates of the setting, infra-red analyses revealed that the dissolution of the hemihydrate in presence of the latex and the hydration of the resultant matrix were less important than for the neat plaster, whatever the type of

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latex.¹⁵ These results were interpreted in terms of the adsorption of the polymer particles onto the plaster grains, which disturbs their dissolution and could hinder their hydration. These phenomena are amplified by the addition of polyamide fibres to the latex-filled plaster blends, as the fibres create a local dehydration, which favours the adsorption of the latex on the hemihydrate.

In the present paper, an investigation of the microstructure of these materials is undertaken with the aim to check the former interpretations. Several microstructures of binary and ternary blends were obtained by adding latexes with varying concentrations to a commercial β -type plaster, and reinforcing with polyamide fibres. Emphasis is put not only on the gypsum crystals morphology, but also on the distributions of the polymer phase and the porosity.

2. Experimental

2.1. Materials

A standard commercial plaster was used for this study: Lutèce 75 from BPB Placo Lambert, Paris, made of 50–70% of β -type hemihydrate (i.e. 50–30% of CaSO_4). The polyamide fibres were provided by Rhodia (research Center at Aubervilliers, France) with different lengths (4, 6, 9 and 18 mm) and two diameters (10 and 19 μm). The latexes were incorporated to the blend from:

- powders: vinyl acetate homopolymer (PA050) or copolymers (PAV22P and PAV30);
- polymer dispersion in water: styrene acrylate copolymer (DS931) or an acrylate ester copolymer (DEC27).

A detailed description of the elaboration process of the neat plaster and the blends (binary and ternary ones) is given in another paper.¹⁵

2.2. Methods

2.2.1. Scanning electron microscopy (SEM)

The surfaces of rupture of the specimens were gold-sputtered and analysed by means of a Philips FEG scanning electron microscope.

2.2.2. Dissolution of the plaster matrix

It is expected that the presence of a continuous polymer film within the mineral matrix may enhance its mechanical and waterproofness properties. So, in order to determine whether the polymer phase shares out as a continuous film, cubic samples of size 30 mm, cut out from the centre of the latex-filled plaster

binary blends, were dipped into hydrochloric acid (HCl, 10N) for 28 days to dissolve the plaster matrix.

2.2.3. Characterization of the porosity

2.2.3.1. Density measurements. The apparent density, ρ , of a specimen is obtained from the ratio of the mass, M , of the sample over its apparent volume, V_{app} . Herein, the apparent density measurements were carried out on parallelepiped samples with dimensions 40 mm \times 40 mm \times 80 mm.

In a blend, the volume fraction of the solid phase, $V_V(\text{S})$, or, equivalently, the volume fraction of the porosity, $V_V(\text{P})$, can be evaluated from the masses and the densities of the gypsum matrix, the latex and the fibres (respectively m_G , m_L , m_F , ρ_G , ρ_L and ρ_F), and their respective volume fractions $V_V(\text{G})$, $V_V(\text{L})$, and $V_V(\text{F})$ using the following two relations:

$$V_V(\text{S}) = V_V(\text{G}) + V_V(\text{L}) + V_V(\text{F}) = 1 - V_V(\text{P}) \quad (1)$$

the volume fraction of a constituent A being defined by:

$$V_V(\text{A}) = \frac{V_A}{V_{\text{APP}}} = \frac{m_A}{M} \frac{\rho}{\rho_A} \quad (2)$$

The mass of the gypsum, m_G , is calculated by assuming that all the hemihydrate is converted into gypsum in the specimen. The mass of the gypsum is then related to the mass of the hemihydrate powder, m_P , and the ratio of their respective molar masses, \mathcal{M}_G and \mathcal{M}_P , by:

$$m_G = m_P \frac{\mathcal{M}_G}{\mathcal{M}_P} \quad (3)$$

The masses m_L and m_F of the additives are unchanged during the elaboration process of the plaster. The densities of the constituents used in this study are reported in Table 1.

2.2.3.2. Mercury porosimetry. This method is based on the injection of a non-wetting fluid, the mercury, in a porous sample initially under vacuum. A pressure is progressively applied to the mercury surrounding the sample. Under a given pressure, only the mercury can intrude the pores with neck sizes above a critical value. The sequence is repeated until a maximum pressure is reached, which corresponds to the fill up of all the pores. The set of pressure steps and the related intruded volumes provide the basic data for pore size distribution calculations. For such information to be generated, the common model depicts the porosity as a system of cylindrical pores, each of which being entirely and equally accessible from the outer surface of the specimen by the surrounding mercury. For porous systems that conform to such a model, the well-known Washburn equation may be properly applied to estimate the diameter of the cylindrical pores intruded

Table 1
Densities of the constituents

	Plaster	Gypsum	Polyamide fibre	Powder-form latexes	Liquid-form latexes	
				PA050; PAV30 and PAV22P	DEC27 type latex	DS931 type latex
Density (g cm^{-3})	1.13	2.32	1.14	0.5	1.04	1.09

at each pressuring step by:

$$d = -\frac{4\gamma \cos \theta}{P} \quad (4)$$

where d is the diameter of the cylinder invaded; γ , the surface tension of mercury; θ , the contact angle of mercury with the solid, and P , the applied pressure.

It must be noticed that the Washburn model commonly used to work out the experimental data (which assumes that the pores are cylindrical and that the mercury can reach completely the pores from the outer surface of the specimen) can not discriminate between a large pore and a set of small pores if both sets are accessible through channels of identical sizes. Thus, the pore size distributions determined by the mercury intrusion method does not afford relevant information on the fraction of large pores and underestimates the mean pore size.

Four to five small samples were cut out from the centre region of standard specimens and dried in an oven at 45 °C until mass stabilisation. A contact angle value of 130° has been used in this study to compute the pore size distribution. Measurements were made in a range of pressure between 0.005 and 200 MPa, which corresponds to a pore size range between 250 and 0.06 μm.

2.2.3.3. Image analysis. This technique has been used to evaluate the size of the macropores (pore size >10 μm). Samples of binary blends containing PAV30 or DEC27-type latex were first embedded in a transparent epoxy resin under vacuum. After hardening of the resin, the obtained cylinders were finely polished by using absolute ethanol for SEM observations. The photomicrographs in grey levels, obtained at low magnification, were transform into binary images where the plaster matrix appears in white colour and the pores in black. The volume fraction of porosity and the pore size distribution were determined on these binary pictures using an in-house software.

3. Results and discussion

3.1. Gypsum crystals morphology

Hydration of plaster results in a crystalline porous product consisting of a tangle of randomly orientated needle-like small crystallites (about 5 μm) and larger particles (Fig. 1a). The addition of polyamide fibres and/or polymer latexes to plaster coarsens the crystallisation (Fig. 1b): the density of the needle-like crystallites is noticeably reduced in comparison to the neat plaster. Moreover, some non-hydrated plaster grains (Fig. 1c) remain in the binary blends, particularly in the materials made of latexes introduced in powder form; some calcium hydroxide Ca(OH)₂ precipitates (Fig. 1d) are formed from the water and the Ca²⁺ ions absorbed by the polyamide fibres, which are dropped during the setting. These results corroborate the disturbance of the plaster hydration by the polyamide fibres and the latexes, as reported in a previous study.¹⁵

However, we also note a reduction of the porosity as the concentration of the latex is increased, due to a partial filling of the voids between the large gypsum crystals by very small ones (Fig. 2a and b). That occurs because of the water-retention

behaviour of the latexes which lengthens the plaster hydration, except for the DS931-type latex for which the structure of the blend is particularly compact due to the important shrinkage during the setting.¹⁶

3.2. Fibre-matrix interface

The fibre-matrix interface consists in loosely bonded gypsum grains in contact with the fibres (Fig. 3a). The surfaces of the fibres totally pulled out of the matrix are either smooth or show a few debris but no obvious marks of strong adhesion (Fig. 3b). The presence of latex in the ternary blends results in a higher density of the contact points between the gypsum crystals and the fibres.

3.3. Polymer phase

3.3.1. Identification

The identification of the polymer phase using SEM is particularly uneasy. However, we have noted in several areas an amorphous phase coating the gypsum crystals and the non-hydrated plaster grains (Fig. 4a and b), and some spherical particles on the pores walls for the plaster/DEC27 latex blends (Fig. 4c). Using energy dispersive X-Ray analysis (EDX) within the SEM, that amorphous phase has been identified with the latex (presence of carbon). Moreover, local analyses have shown the presence of a polymer film (Fig. 4d), particularly in the ternary blends, which could result from a coalescence of the latex particles once the water around was absorbed by the fibres.

3.3.2. Structure of the polymer film

The specimens containing latexes introduced in the form of powder completely dissolve when dipped for 28 days in hydrochloric acid, whatever the polymer concentration. That means the polymer film is not organized in a continuous structure within the gypsum. Unlikely, the specimens made with the latexes introduced in a liquid form at concentrations higher than 2.5 wt.% do not crumble after a long stay in hydrochloric acid: a continuous polymer film is set, which preserves the initial geometry of the specimen. That threshold value of 2.5 wt.% for the latex to form a continuous film within the plaster matrix is in agreement with the reports in the literature for mortar/latex blends.^{17,18}

3.4. Investigation of the porosity

In a set plaster, the porosity ranges from a few tenths of micrometers for the voids between the gypsum crystals up to some millimetres for the air bubbles trapped during the mixing. In the aim to discriminate all the types of porosity in these blends, we have made use of several techniques: density measurements, mercury intrusion and image analysis. The first method was applied for all the materials, while the two others were used only for the plaster/latex binary blends because the specimen preparation method is incompatible with the presence of fibres.

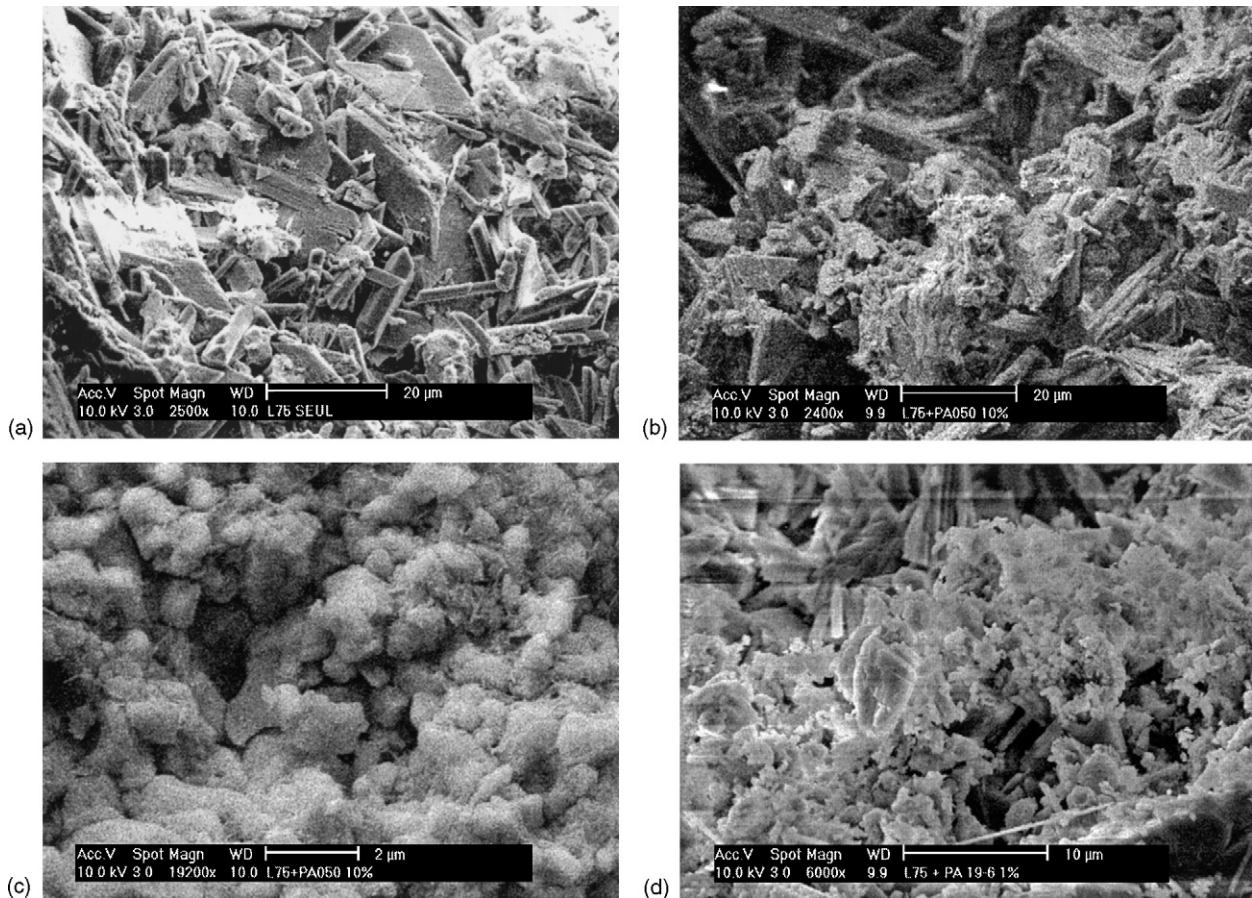


Fig. 1. Photomicrographs of the gypsum crystals in (a) the neat plaster; (b) a plaster/PA050 type latex blend; (c) non-hydrated plaster grains in a plaster/PA050 type latex blend; (d) calcium hydroxide precipitates in a polyamide fibre/plaster blend.

3.4.1. Total porosity from density measurements

The pore volume fraction in the neat plaster, determined from the density measurements is 51.12%, which is similar to the value reported in the literature (50 vol.% for a mixing ratio of 0.68, as determined by the mercury intrusion method).¹⁹

The evolution of the total porosity of the binary and ternary blends as a function of the concentration of the additives is shown in Fig. 5a–c. The same upward trend towards a plateau value of porosity is observed with the concentration of fibres, except

for the shortest fibres (4 mm). Unlike the fibres, the addition of polymer latexes reduces the total porosity due to a partial fill up of the pores by the latex particles. But the major contribution to the reduction of the porosity may be the fill up of the voids between the gypsum crystals by very small ones, as revealed by the SEM observations of the plaster–latex blends reported above (Fig. 2). The important reduction of the porosity of the blends with high amounts of the DS931-type latex is correlated to the pronounced shrinkage (>25%) noted during the setting.¹⁶

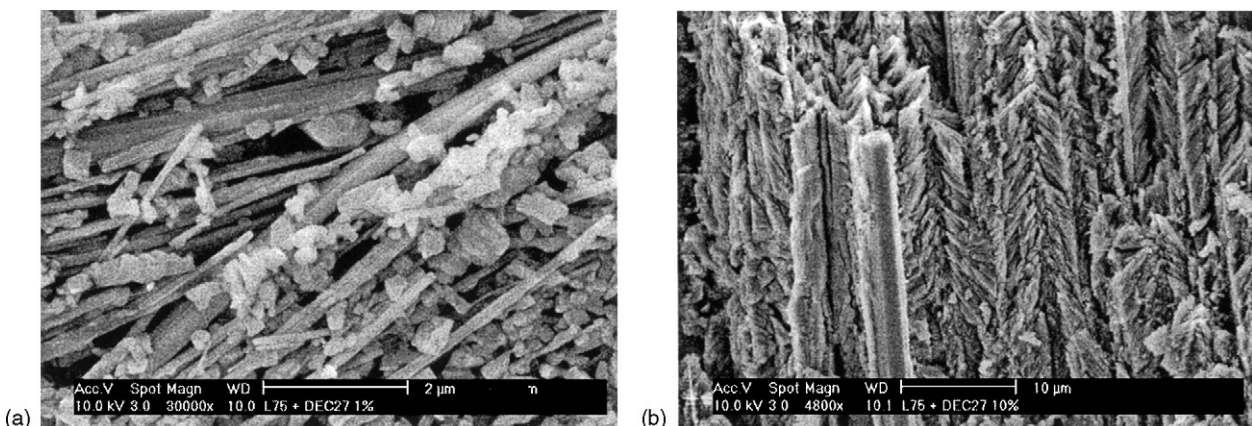


Fig. 2. Fine gypsum crystals developed within the initial crystalline network in plaster/DEC27-type latex blends containing 1 wt.% (a) and 10 wt.% (b) of latex.

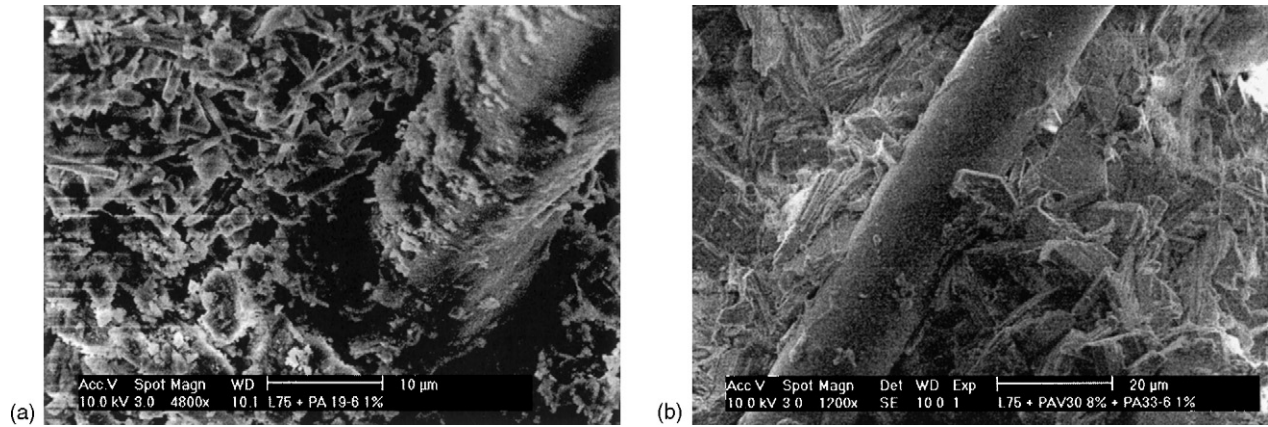


Fig. 3. Fibre-matrix interface (a) and fibre pulled out from the matrix (b).

The issue concerning the adverse influences of the polyamide fibres and the latexes on the total porosity is depicted in Fig. 5c for the ternary blends containing the PAV30-type polymer. It appears that for a given concentration of fibres, the total porosity can be noticeably depressed by the addition of the latex. As an example, a 11 vol.% reduction of the porosity is achieved by the addition of 8 wt.% of the PAV30-type latex, while the decrease is 14 vol.% for the same concentration of latex in the plaster/fibre binary blend. That means that the latex contributes to reduce the

porosity of the ternary blends by partially filling up the pores, but does not act to reduce the porosity induced by the fibres (gaps at the fibre-matrix interface, porosity due to the rough dispersion of the longest fibres).

3.4.2. Porosity investigation by mercury intrusion

The determination of the porosity from density measurements gives a global value of the porosity but cannot afford an insight on the pore size distribution. The mercury intrusion method was

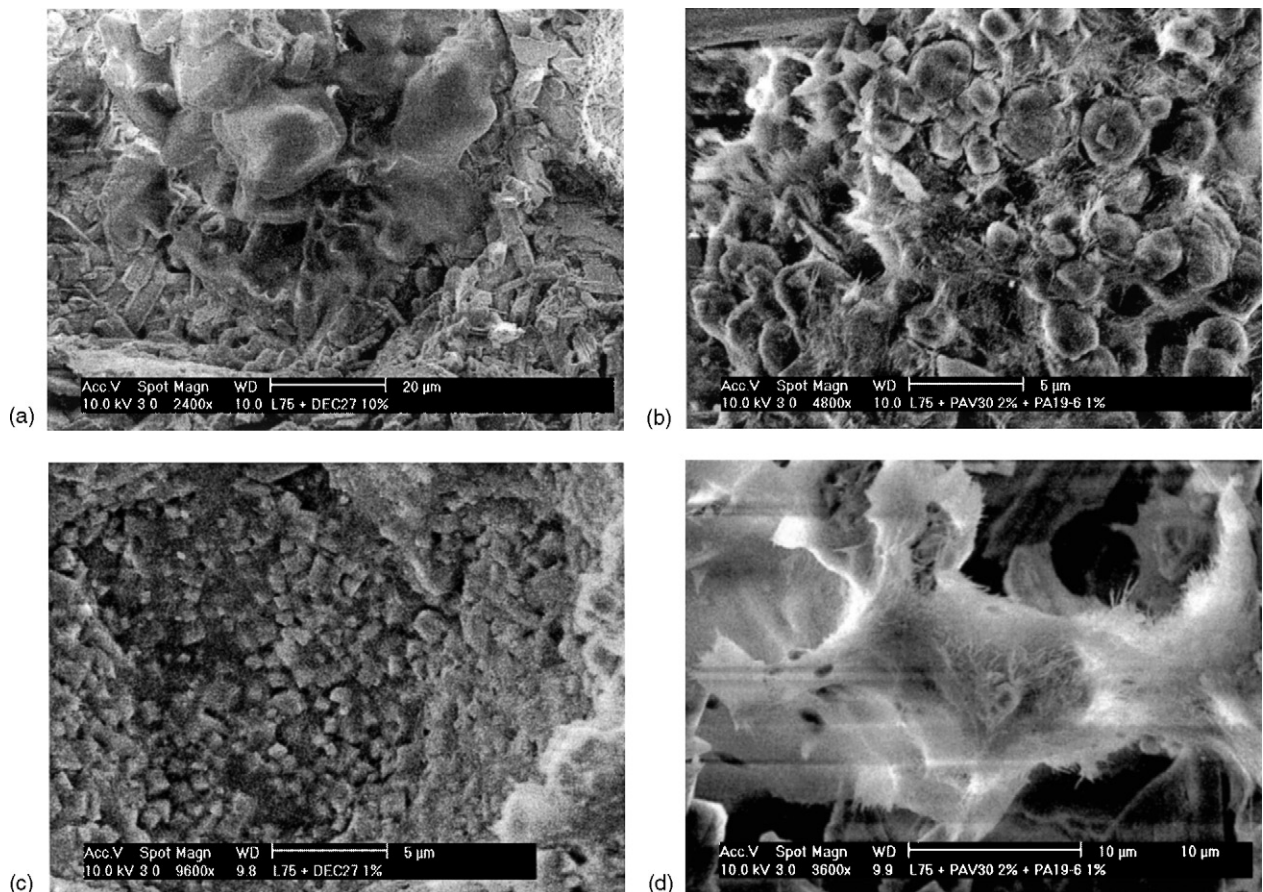


Fig. 4. Evidences of (a) an amorphous phase coating the gypsum crystals and (b) non-hydrated plaster grains. Aspects of (c) the pore walls in plaster/latex blends; (d) the polymer film.

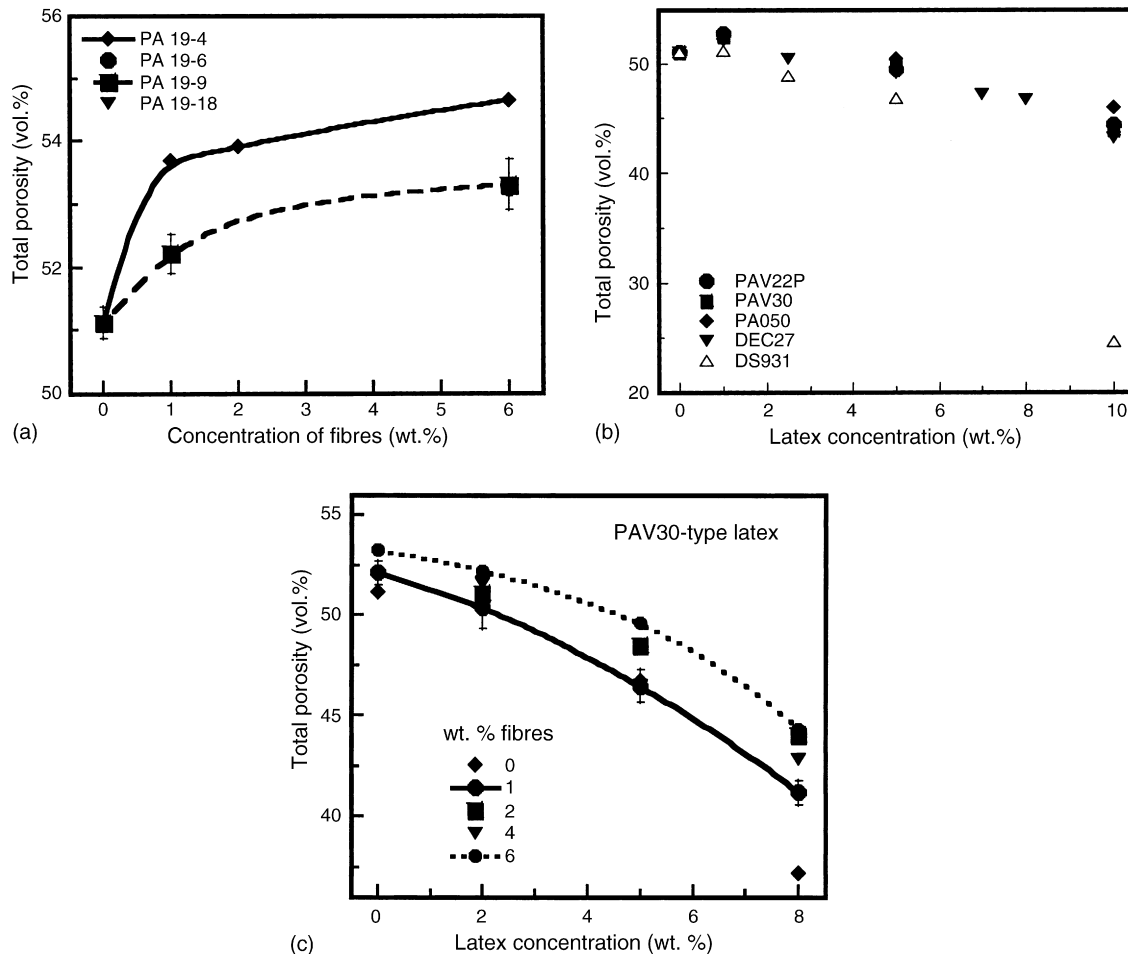


Fig. 5. Evolution of the total porosity of the blends: (a) plaster/polyamide fibre; (b) plaster/latex; (c) ternary blends.

then used to examine the relative importance of the different types of pores.

3.4.2.1. Total porosity. The porosity of the neat plaster, determined by mercury intrusion, is 51.98 vol.%, which is almost identical to the value (51.12 vol.%) determined from density measurements.

In Fig. 6a, the evolution of the porosity of the blends containing PAV30 or DEC27-type latex shows the same downward trend as a function of the latex concentration. Moreover, a good agreement is observed between the two sets of values obtained by the density measurements and the mercury intrusion method (Fig. 6b). These results confirm that the hydration of the plaster is almost complete, at least for low latex concentrations.

3.4.2.2. Pore size distributions. In Fig. 7a are shown the pore size distributions determined by the mercury intrusion method, in the neat plaster and in plaster/latex blends containing 10 wt.% of the two types of latex (the intermediate concentrations 1 and 5 wt.% are omitted for the sake of clarity). In these distributions it appears that the contribution of the capillary porosity of plaster is only slightly modified by the presence of latex. Contrarily, the contribution of the inter-laminate porosity, with a size

range comparable to the latex particle diameters, is significantly increased.

3.4.2.3. Residual trapped mercury. In the course of a mercury intrusion test, the volume of intruded mercury represents the total accessible porosity of the sample. When carrying out a withdrawal of the mercury after the maximal pressure is reached (the pressure is progressively released following the same pressure-time path as in the input stage), a fraction of the intruded volume of mercury may be retained within the sample. The porosity related to that volume of trapped mercury is referred to as the “trapped porosity”.

The evolution of this trapped porosity as a function of the latex concentration is presented in Fig. 8a and b for the PAV30 or DEC27-type latexes blends. In the two cases, the percentage of trapped porosity is important and shows an inverted trend in comparison with the total porosity. It increases regularly with the latex concentration in the case of the PAV30 while, for the DEC27 it corresponds almost to the global porosity for latex concentrations above 2 wt.%.

This marked difference of behaviour between the PAV30 and DEC27 samples is in agreement with dissolution experiments in hydrochloric acid.¹⁵ In the DEC27 case, a continuous latex film develops within the mineral structure for latex concentrations above 2 wt.%, which prevents the blend to collapse when

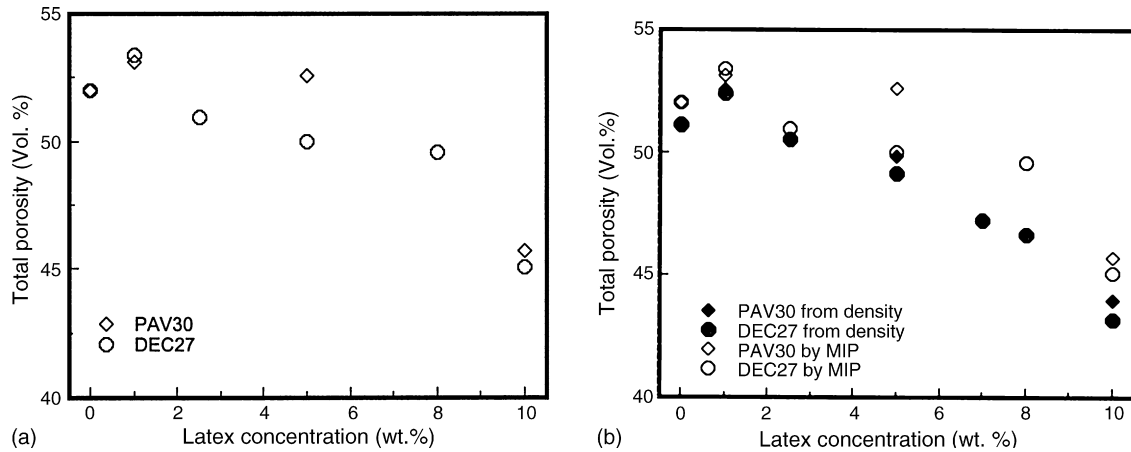


Fig. 6. (a) Total porosity determined by mercury intrusion for the blends containing PAV30 or DEC27-type latex; (b) comparison with density measurements.

plunged in hydrochloric acid. That film drastically reduces the throats sizes which give access to the pores.

3.4.3. Porosity evaluated by image analysis

The macroporosity of the plaster/latex blends was investigated by image analysis on SEM photomicrographs in grey levels, obtained at low magnification, as presented in Fig. 9a and b.

The porosity values reported in Table 2a are obviously lower than those determined from density or mercury intrusion measurements. That discrepancy is explained by the fact that only the macroporosity (not the inter-crystallite and inter-laminate porosity) is considered by image analysis, due to the used magnification. From these results, it can be stated that the macroporosity constitutes about half the total porosity of the blends. Moreover, neither the macroporosity nor the mean pore size

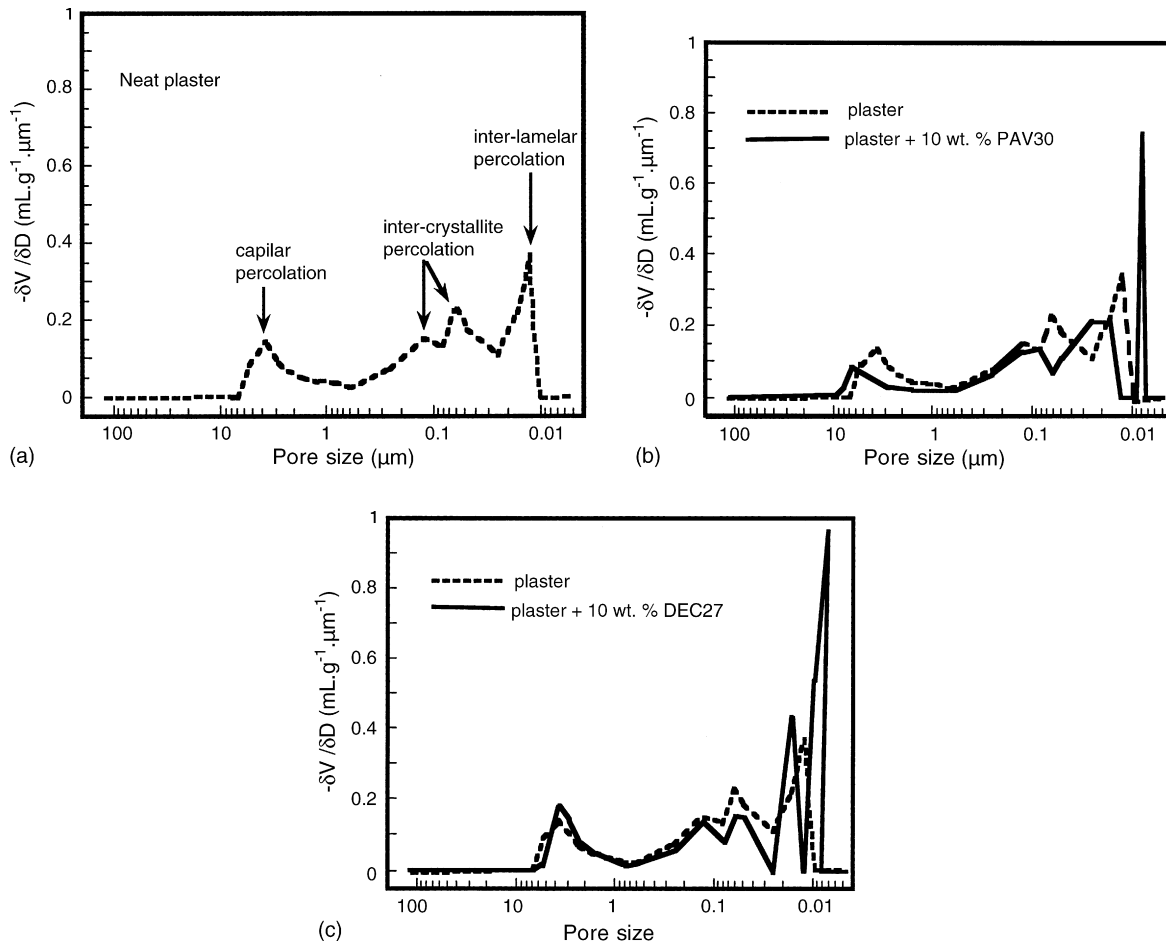


Fig. 7. Pore size distributions in the neat plaster (a); in plaster/latex blends containing PAV30 (b) and DEC27 (c) type latex.

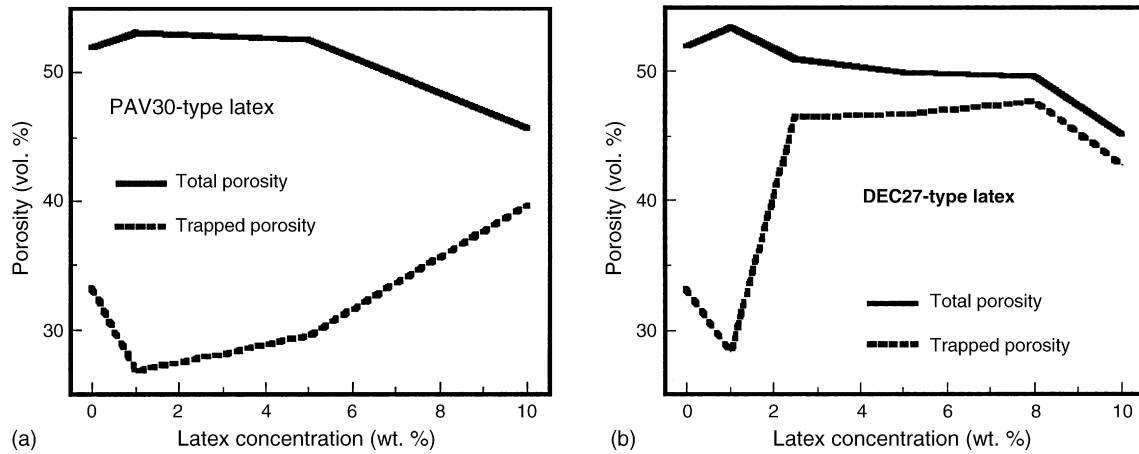


Fig. 8. Evolution of the total and trapped porosities for the binary blends, as a function of the concentration of (a) PAV30 and (b) DEC27-type latex.

Table 2a

Porosity of plaster/latex blends measured on SEM photomicrographs by image analysis

Latex concentration (wt.%)	Plaster/PAV30 latex (vol.%)	Plaster/DEC27 latex (vol.%)
0	24.70	24.70
1	23.64	25.37
5	18.99	25.33
10	30.73	25.70

Table 2b

Mean free path within the pores in plaster/latex blends, measured on SEM photomicrographs by image analysis

Latex concentration (wt.%)	Plaster/PAV30 latex (μm)	Plaster/DEC27 latex (μm)
0	32.59	32.59
1	37.92	41.69
5	37.14	27.53
10	48.11	36.50

(Table 2b) is significantly modified by the addition of increasing amounts of latex. Therefore, it is concluded that (i) the air drawing effect often associated with latexes in mortar is not observed when the polymer is mixed with plaster, and (ii) the

addition of the latex does not affect the macroporosity of plaster as the pore sizes are much larger than the diameter of the latex particles.

4. Concluding remarks

The influence of polyamide fibres and the polymer latexes on the microstructure of plaster have been investigated. The addition of polyamide fibres and/or polymer latexes to plaster results in a coarser crystallisation, and disturbs the hydration of plaster, as non hydrated plaster grains and precipitates of calcium hydroxide $\text{Ca}(\text{OH})_2$ are observed.

The polymer latex coats the gypsum grains and the non-hydrated plaster grains, and contributes to ameliorate the compactness of the blends. Only the latexes introduced in liquid form spreads in a continuous film when the concentration exceeds 2.5 wt.%.

Association of polyamide fibres to plaster increases the porosity. Conversely, an important reduction of the porosity with the latex concentration is noted: the ternary blends are less porous than the binary plaster/fibres blends. Measurements by mercury intrusion and image analysis show that the macroporosity and the capillary porosity of the plaster are not modified by the presence of the latex. The latex fills up the inter-crystallite

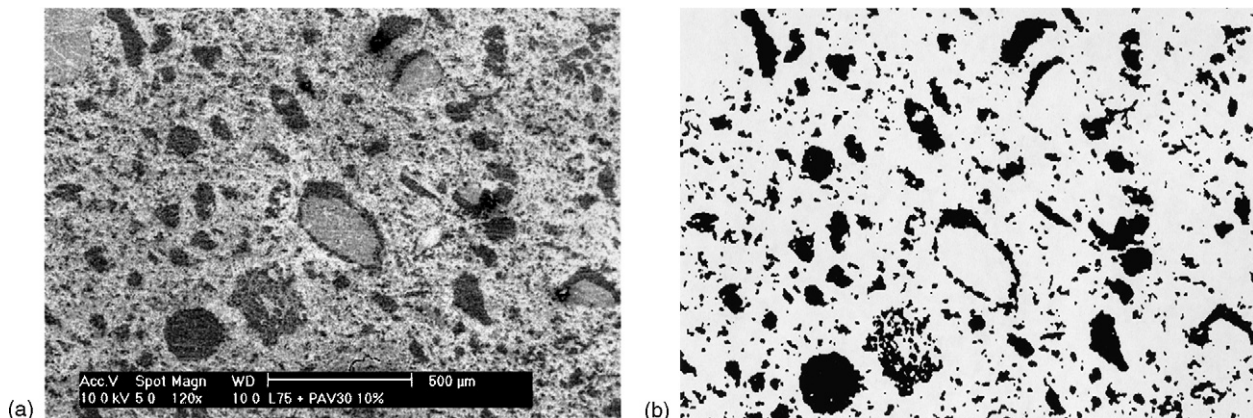


Fig. 9. SEM photomicrograph of the polished surface of a plaster/10 wt.% PAV30 blend (a); associated binary image.

and inter-laminate pores, whose dimensions are similar to the latex particles sizes, modifying the accessibility to the porous network.

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