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Microstructure of latex-filled plaster composites

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Abstract

We have investigated the effects of the nature and the concentration of latex on the microstructure of plaster/polymer blends in terms of the gypsum crystals morphology, the distribution of the polymer phase and the porosity of the materials. Addition of latexes to plaster results in a coarser crystallisation, a disturbance of the plaster hydration and a higher porosity. These changes are the more pronounced so as the concentration of latex is high. It is shown that the presence of latex noticeably modifies the porous network of the plaster.

Keywords: Gypsum–Latex; Composites; Microstructure-final; Porosity; Electron Microscopy

1. Introduction

In a previous study,[1] we had investigated the setting of polymer latex/plaster and polyamide fibre/plaster binary blends and plaster/latex/fibres ternary blends. The results clearly showed an influence of the nature of the latex on the setting of the plaster: for the latex containing a water-repellent component the setting of the plaster was strongly delayed, while the other types of latex do not increase the setting time or only lightly. Moreover, 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 latex.[1] 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.

In the present paper, an investigation of the microstructure of latex-filled plaster materials is undertaken with the aim to check the former interpretations. Several microstructures of binary blends were obtained by adding latexes with varying concentrations to a commercial β-type plaster. 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 CaSO4). The latexes, provided by Rhodia (Research Center at Aubervilliers, France), were incorporated to the blend from:

- powders: vinyl acetate homopolymer (PA050) or copolymers (PAV22P and PAV30);
- polymer dispersions 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 is given in another paper.[1]

2.2. Methods

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

It is expected that the presence of a continuous polymer film within the mineral matrix may enhance its mechanical and waterproofness properties. Such a beneficial effect was reported by Justnes and Øye[2] for latex–cement composites. In order to determine whether the polymer phase shared out as a continuous film,

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bits of specimens were etched with hydrochloric acid. We have dipped cubic samples of size 30 mm, cut out from the centre of the latex-filled plaster binary blends, into hydrochloric acid (HCl, 10 N) for 28 days to dissolve the plaster matrix.

The total porosity and the trapped porosity were measured by using the mercury intrusion method applied by Diamond[3] to assess the microstructure of hydraulic binders. Four to five small samples were cut in 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.

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 polymer latexes to plaster coarsens the crystallisation and some non-hydrated plaster grains (Fig. 1b) remain, particularly in the materials made of latexes introduced in powder form. These results corroborate the disturbance of the plaster hydration by the polyamide fibres and the latexes, as reported in a previous study.[1]

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.[1]

3.2. Identification and structure of the polymer phase

The identification of the polymer phase using SEM is particularly uneasy. However, we have noted in several areas an amorphous phase (identified with latex by using energy dis-

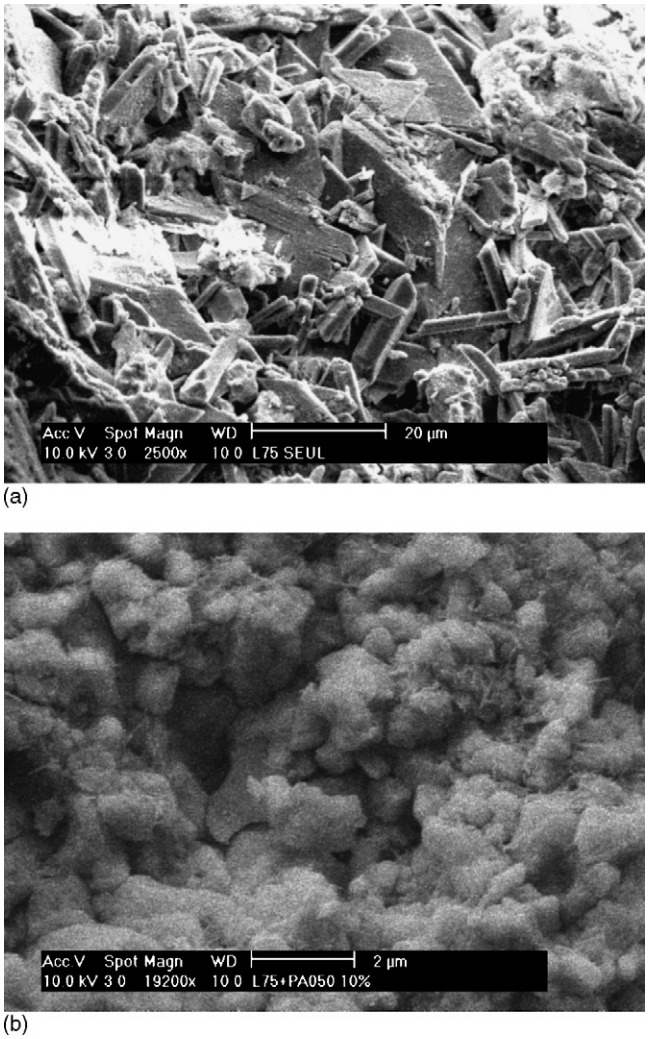

Fig. 1. Photomicrographs of the gypsum crystals in: (a) the neat plaster and (b) non-hydrated plaster grains in a plaster/PA050 type latex blend.

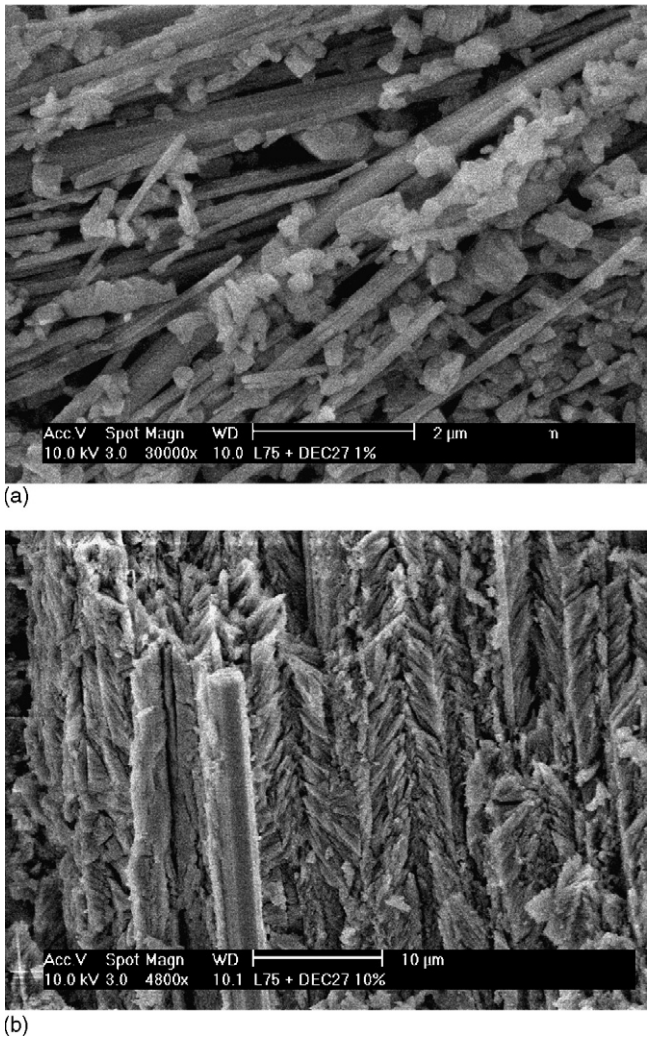

Fig. 2. Fine gypsum crystals developed within the initial crystalline network in plaster/DEC27-type latex blends containing 1 wt.% (a) and 10 wt.% (b) of latex.

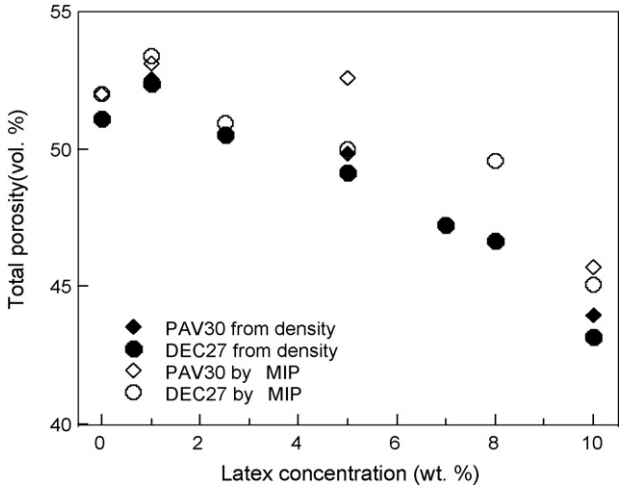

Fig. 3. Comparison of the total porosity determined by mercury intrusion for the blends containing PAV30 or DEC27-type latex with calculated data assuming a full hydration.

persive X-ray analysis) coating the gypsum crystals and the non-hydrated plaster grains.

The specimens containing latexes introduced in the form of powder can completely dissolve when dipped for 28 days in hydrochloric acid (10 M), 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.[2,4]

3.3. Porosity investigation by mercury intrusion

The total 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. For a consistency of 0.68, Coquard[5] reported a total porosity of about 50 vol.%.

In Fig. 3 the evolution of the porosity of the blends containing PAV30 or DEC27-type latex shows the same downwards trend as a function of the latex concentration. That feature was reported by different authors for latex–cements blends.[6–8] Moreover, a good agreement is observed between the two sets of values obtained by the density measurements and the mercury intrusion method. These results confirm that the hydration of

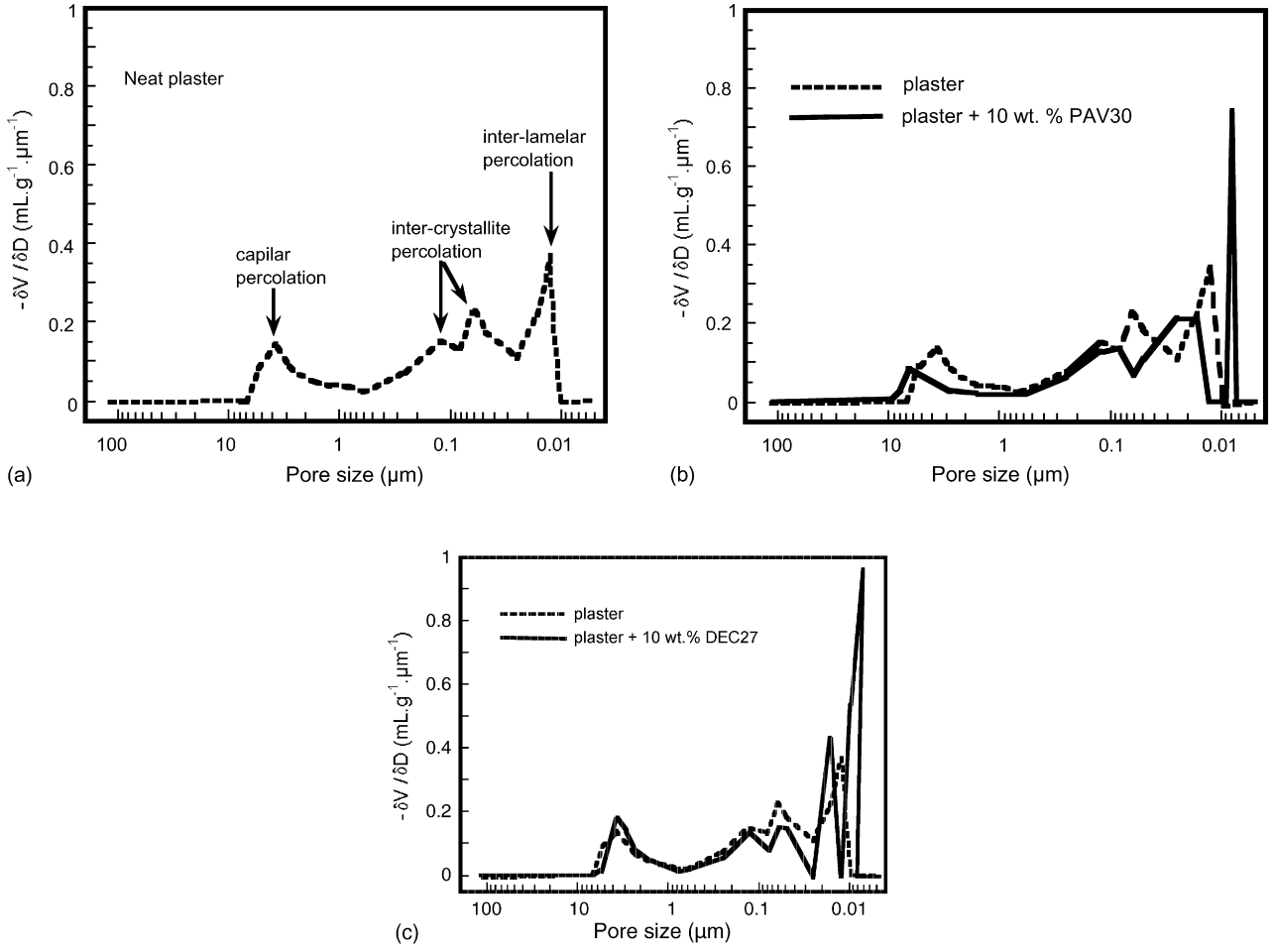

Fig. 4. Pore size distributions in the neat plaster (a), in plaster/latex blends containing different concentrations of PAV30 (b) and DEC27 (c) type latex.

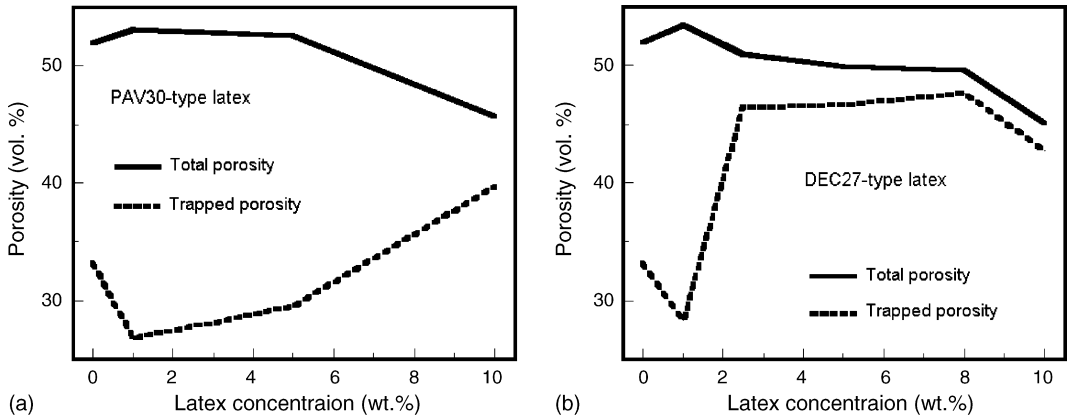

Fig. 5. Evolution of the total and trapped porosities for the binary blends, as a function of the concentration of (a) PAV30 and (b) DEC27-type latex.

the plaster is almost complete, at least for low latex concentrations. DEC27-type latex with calculated data assuming a full hydration.

In Fig. 4a–c we show 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 part corresponding to 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.

Residual trapped fluid: 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. 5a 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. 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 plunged in hydrochloric acid. That film drastically reduces the throats sizes which give access to the pores.

4. Concluding remarks

The influence of polymer latexes on the microstructure of plaster has been investigated. The addition of latexes to plaster results in a coarser crystallisation, and disturbs the hydration of plaster, as non-hydrated plaster grains 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 spread in a continuous film when the concentration exceeds 2.5 wt.%. An important reduction of the porosity with the latex concentration is noted; 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 and inter-laminate pores, whose dimensions are similar to the latex particles sizes, modifying the topology to the porous network.

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