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High-pressure epoxy-impregnated cementitious materials for microstructure characterization

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Abstract

High-pressure fluorescent epoxy impregnation (> 20 bar) of cement-based materials is compared to the more conventional method of vacuum impregnation. Parameters such as the epoxy resin penetration depth and the stability of the fluorescence intensity are evaluated in order to determine the effectiveness and reliability of the aforementioned methods in preparing paste and mortar samples for microstructure characterization. An evaluation of polymer loading as a function of impregnation pressure reveals a saturation pressure (P_{sat}) at which complete filling of the pores is achieved. The evolution of the fluorescent epoxy resin penetration front is examined under ultraviolet (UV) light, and correlated to the impregnation pressure. Results clearly indicate that high-pressure impregnation is a more effective and faster method to imbed epoxy resin in cementitious materials. Furthermore, P_{sat} is a parameter that is sensitive to a material's microstructure, particularly in pastes samples of high water-to-cement ratios (W/C) which reveal a polymer overloading point. Fluorescence stability of the high-pressure-impregnated sample is compared to that of the vacuum-impregnated sample. Results show that the high-pressure-impregnated samples have a higher intensity and stability. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The process of impregnating the pores of cementitious materials with low-viscosity epoxy resin is a common sample preparation method for microscopic quantitative evaluation (porosity and size distribution) and structural characterization (geometry and connectivity). Cementitious microstructure is often examined with techniques such as transmitted light microscopy [1–3] and SEM [4–7], which require the preparation of epoxy-impregnated samples. The presence of the epoxy resin supports the fragile pores and matrix phases during the different stages of preparation: grinding and polishing. Furthermore, the presence of the epoxy resin facilitates the identification of pores by providing optical or atomic number contrast with respect to the other phases present in the microstructure. Vacuum impregnation is the most widely adopted method for preparing cement paste, mortar and concrete samples for microscopic investigation. However, alternative methods such as pressure impregnation and epoxy–solvent replacement [8] are also adopted. The preference for the vacuum process is due to the fact that the process is less expensive and readily available with traditional pumps and chambers. However, the vacuum impregnation method results in excessive drying of the sample, and therefore cracks are introduced during sample preparation. On the other hand, the epoxy–solvent replacement technique eliminates this latter problem, but requires long sample preparation times. The pressure technique, however, shows distinct advantages such as higher tensile and flexural strength samples in comparison to samples of the vacuum process at similar polymer loading [9–11], implying higher stability of the cementitious specimen during the preparation phases. However, no reports clearly show or address the issue of the introduction of cracks during sample impregnation.

What is truly noteworthy about these investigations (and pressure impregnation studies in general) is that operation is almost exclusively in the pressure range of 10 to 20 bar [12]. As far as the authors are aware, there have not been any rigorous investigations above the generally accepted limit of 20 bar. Therefore, the scope of this study is the characterization of epoxy-reinforced cementitious compo-

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sites impregnated in the pressure range above 20 bar, a range that will be termed the "high"-pressure range. Furthermore, visualization of the developing impregnation front (or equivalently, the polymer penetration depth) is performed by a combined process of sectioning and ultraviolet (UV) fluorescence imaging. In addition, vacuum-impregnated samples are also prepared, and the effectiveness of vacuum- and high-pressure-impregnated methods is compared. Transmitted light microscopy is carried out on the vacuum- and high-pressure-impregnated thin-section samples in order to evaluate the intensity and stability of the fluorescence.

2. Experimental procedure

2.1. Cementitious materials

The composition of the cement-based materials studied in this investigation are summarized in Table 1: pastes of water-to-cement ratio (W/C) 0.3, 0.5, and 0.6, and two types of mortars—a norm mortar (NM) and a fine sand mortar (FM) both having W/C = 0.50. The cement used is a Type I Portland Cement.

Paste samples are mixed for 5 min in a standard planetary mixer and cast in plastic vials (diameter = 2.5 cm, height = 5.0 cm), while mortar samples are prepared according to the procedure outlined in the *European Norm (EN) 196—Part 1* and cast into rectangular prisms using steel molds. All samples are demolded after 24 h under ambient conditions and cured in a saturated lime solution for 6 days prior to impregnation.

2.2. High-pressure epoxy impregnation

Paste samples are cut with a diamond saw into smaller cylinders of diameter = 2.4 cm and height = 1.5 cm, whereas mortar samples are cut into 2 × 2 × 1.5 cm prisms. The paste and mortar samples are then dried for 2 days at a temperature of 80 °C in an air-circulating oven. Following the drying period, the samples are allowed to cool down to room temperature prior to being impregnated with the epoxy resin.

The test set-up consisting of a steel cylinder and a hydraulic piston is used to epoxy impregnate samples at pressures of 10, 20, 50, 80, 100, 200 and 400 bar. A commercially available two-component, low-viscosity epoxy is used for the impregnation of the samples. In order to view the samples under UV light, fluorescent dye is added to the epoxy at a quantity of 0.0275% based on the weight of the polymer resin.

Table 1
Composition of cementitious materials used in the investigation

Sample ID	Cement (g)	Water (g)	Aggregate (g)	W/C
P03 (paste)	1000	300	0	0.30
P05 (paste)	1000	500	0	0.50
P06 (paste)	1000	600	0	0.60
NM (mortar)	450	225	1350 (Norm sand)	0.50
FM (mortar)	450	225	1350 (Fine sand, < 1.0 mm)	0.50

Mortar and paste samples are placed in a steel cylinder that is tightly sealed at the bottom with a Teflon block. The steel cylinder is then filled with epoxy up to a designated level that ensures coverage of the specimens by a column of polymer resin at least 5 cm higher than the top surface of the specimens. Another Teflon block is then used to tightly seal the top of the steel cylinder. Pressure is then applied to the top Teflon block, and consequently to the contents of the cylinder, through a hydraulic piston. Samples are loaded up to the desired pressure, and held under constant pressure for 90 min. The pressure is then released, and samples removed from the steel cylinder. Curing of the epoxy-impregnated samples is carried out at 50 °C in a closed oven for 24 h until the epoxy resin is hardened.

Specimen weights are recorded prior to (dry wt.), and after impregnation (loaded wt.) in order to determine the polymer loading which is defined as (Eq. (1)):

$$\text{polymer loading (\%)} = (\text{loaded wt.} - \text{dry wt.})/\text{dry wt.} \times 100 \qquad (1)$$

2.3. Characterization of impregnation depth: sequential sectioning

Impregnated paste and mortar samples are sectioned perpendicularly to the axial direction to yield six distinct cross-sections each separated by 2 mm from its neighbor (see Fig. 1). Cuts are taken at the direct middle (central portion) of the sample (0 mm), and then at ± 2 and ± 4 mm from the midline. Sections are labeled from 0 to 5 with the surface most distant from the exposed surface (Fig. 1) of each section used as the examined surface. Samples are viewed in a Camag UV-box with wavelength, $\lambda = 254$ nm, and digital images are acquired through a digital camera.

2.4. Vacuum epoxy impregnation

In order to compare the high-pressure-impregnated samples to those prepared by the more frequently utilized methods, paste samples of extreme W/C (0.3 and 0.6) and a NM are vacuum-impregnated according the procedure described below:

(a) Paste and mortar cross-sections having a thickness between 2 and 3 mm are obtained using a diamond saw.
(b) The samples are then dried in an air-circulating oven at a temperature of 80 °C for 24 h.
(c) Then, the samples are placed in individual sample holders and evacuated for at least 6 h at a constant pressure of 8 mbar in a vacuum chamber.

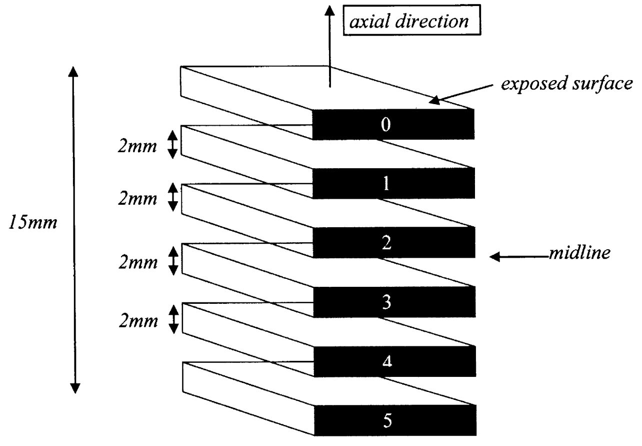

Fig. 1. Schematic diagram showing the sectioning procedure for mortar specimens (paste samples are done in the same manner except that the sections are discs instead of prisms).

(d) The sample holders are then filled with the epoxy resin that is introduced into the chamber while maintaining the vacuum.
(e) The samples, submerged by the epoxy resin, are kept under vacuum for an additional 15 min.
(f) Finally, the samples are removed from the vacuum chamber, and cured in a closed oven for 24 h at a temperature of 80 °C.

Sequential sectioning of the vacuum-impregnated samples is not performed due to their small thickness (2 to 3 mm). Instead, a thin layer of excess polymer material on the surfaces is removed through grinding. Similar to the high-pressure impregnation samples, digital pictures are obtained for the vacuum-impregnated samples under exposure to UV light.

2.5. Microscopy

Optical microscopy, more specifically fluorescence microscopy using UV light, is used to examine the quality of the impregnated samples. It is well known that fluorescent dye embedded in epoxy resin loses intensity upon exposure to UV light during microscopic observation. Therefore, the stability of the impregnated fluorescent dye is monitored in thin-section specimens at different times while exposed to UV light. The latter is achieved through the measurement of the exposure time at different time intervals, in transmission mode, by a light meter controlling a camera shutter. The exposure time is defined as the time required for a determined/critical amount of photons to be collected by a detector which then instructs an automatic image acquisition system to close the shutter of a camera. Thus, the intensity is inversely related to exposure time required to collect a determined amount of photons. A shorter and invariant exposure time is an indication of higher sample intensity and stability, respectively. The uncertainty of the exposure time measurements is of the order of ±0.5 s.

3. Results and discussion

3.1. Polymer loading vs. impregnation pressure (high range)

The three paste samples (P03, P0, and P06) and the two mortars (NM and FM), as previously mentioned, are impregnated at pressures of 10, 20, 50, 80, 100, 200 and 400 bar. The polymer loading for each sample is plotted as a function of impregnation pressure in Fig. 2. The trend shown by the curves in Fig. 2 indicates the existence of a saturation pressure (P_{sat}-delineated by the dashed line in Fig. 2); that is, there exists an impregnation pressure above which further penetration of the epoxy resin into the material is invariant. It is assumed that once the saturation pressure is reached, complete filling of the accessible pores is achieved. Thus, further increases in impregnation pressure results in a constant polymer loading. Of course, P_{sat} will be different for cementitious samples of different compositions due to differences in porosity (structure, quantity and its distribution) and aggregates (size and particle size distribution).

In Fig. 2, it is shown that the paste sample with the highest W/C also exhibits the highest percentage of polymer loading, which is consistent with the notion that a higher W/C implies higher porosity. However, the graph in Fig. 2 also shows that paste sample P06 (W/C = 0.6) and, to a lesser extent, paste sample P05 (W/C = 0.5), undergoes a *polymer overloading* at a pressure above 20 bar that exceeds the polymer loading observed at P_{sat} and thereafter. The polymer overloading can be attributed to the material strength (i.e., pore structure). Fig. 3 is a picture of a cross-section cut parallel to the

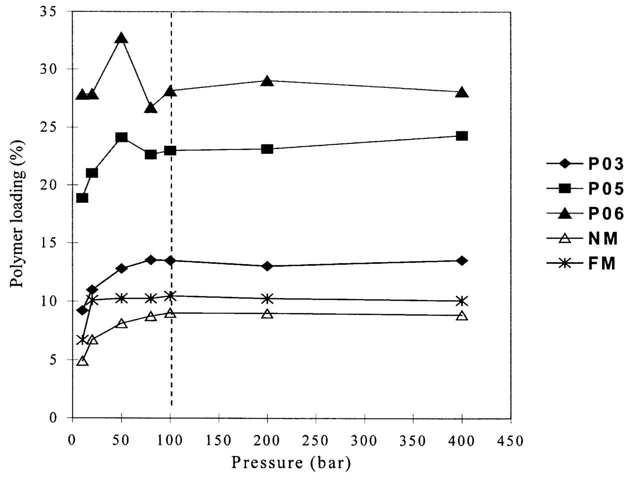

Fig. 2. Polymer loading for the paste samples P03, P05, P06 (W/C = 0.30, 0.50, and 0.6, respectively) and the mortars samples NM and FM (W/C = 0.50). The vertical line represents P_{sat} = 100 bar.

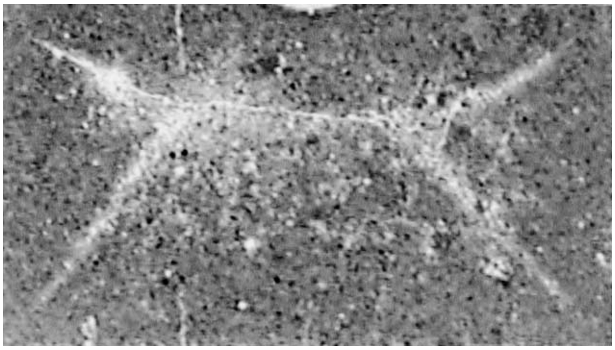

Fig. 3. Compressive failure patterns observed in high-pressure impregnation of sample P06 (W/C = 0.6).

direction of applied axial pressure (see Fig. 1) of a W/C = 0.6 paste specimen (P06). The observed pattern is an indication of compressive failure resulting from the applied pressure. Thus, the polymer overloading is most likely explained by facilitated and enhanced epoxy penetration by the failure of the weakest pores. Once the sample is impregnated at pressures above the overloading point, the material is no longer able to sustain the loads and failure occurs along the planes of highest shear stress. Given the hydrostatic state of stress, an increase in pressure causes the paste sample to collapse on itself closing the cracked surfaces, and thereby decreasing the material polymer loading capacity. Indeed, beyond a pressure of 100 bar, the polymer loading of paste sample P06 remains relatively constant. Consequently, paste sample P05 (W/C = 0.5) is stronger than P06 (W/C = 0.6), and it does not exhibit severe polymer overloading.

On the other hand, the two mortars, namely, NM and FM, have different polymer loading behaviors despite the fact that the aggregate-to-cement ratio and W/C of both samples are identical. Fresh air content measurements indicate that NM has a lower air content (3.0%) than FM (air content = 5.5%). Thus, the FM sample exhibits a higher percentage of polymer loading due to its more porous structure.

The less porous samples such as the 0.3 paste and the NM exhibit a gradual rise towards a P_{sat} of 100 bar. Whereas the FM, due its porosity, achieves saturation after a pressure of 20 bar, but did not show an overloading point. As indicated by the dashed line in Fig. 2, the samples used in this investigation suggest that an impregnation pressure of 100 bar represents an appropriate impregnation pressure (one that is neither too low for partial pore filling nor too excessive to cause compressive failure) for low to typical W/C pastes (0.3 to 0.45) and mortars. However, lower pressures (50 bar or less) are more suitable for pastes of high W/C.

3.2. Degree of polymer impregnation: high pressure vs. vacuum impregnation

One of the cited problems with polymer-impregnated cementitious materials is the lack of a reliable and convenient method to measure the polymer impregnation depth [3]. In any microscopic preparation, it is important to take cross-sections that have been fully invaded with epoxy to prevent microstructure damage during grinding and polishing. Furthermore, for fluorescence microscopy, it is critical to have samples that exhibit uniform, stable, as well as sufficient intensity for microstructural characterization. The cross-sectional images viewed under UV light in Fig. 4 dramatically show the evolution of the penetration front as a function of pressure. Note the distinct polymer-impregnated rims (bright gray areas) and the nonimpregnated cores (darker areas) in the 10- and 20-bar samples.

Moreover, the penetration front disappears at 100 bar resulting in a uniformly fluorescing sample. This finding is in direct correlation with the polymer loading curve in Fig. 2, which expects a fully loaded sample at 100 bar for the samples that do not exhibit polymer overloading.

As previously mentioned, vacuum-impregnated samples are also prepared in order to compare them to the high-pressure-impregnated samples. Digital images of the vacuum-impregnated samples (paste—0.3 and 0.6; NM) are shown in Fig. 5. Notice that only a small fraction of the pores are filled when the NM sample when subjected to

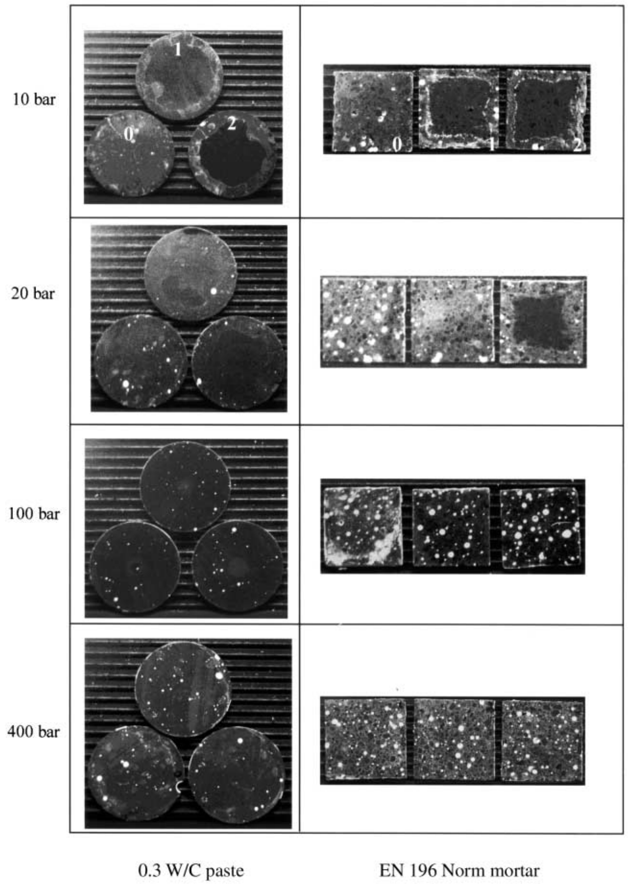

Fig. 4. Cross-section of 0.3 W/C paste and NM samples viewed under UV light. Only Sections 0, 1, and 2 (refer to Fig. 1) are shown for each sample (see 10-bar samples for numbering scheme). Note the presence of a distinct penetration front in the 10- and 20-bar samples and the elimination of the front at 100 bar.

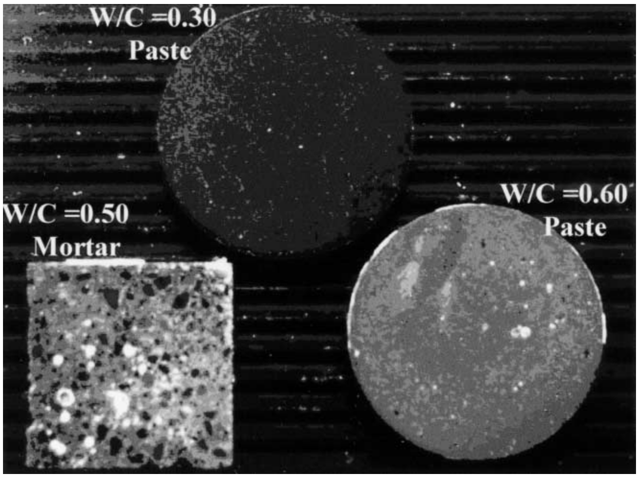

Fig. 5. Cross-sections of vacuum-impregnated pastes (0.3 and 0.6) and NM samples viewed under UV light. Note the incomplete filling of the pores by the epoxy resin.

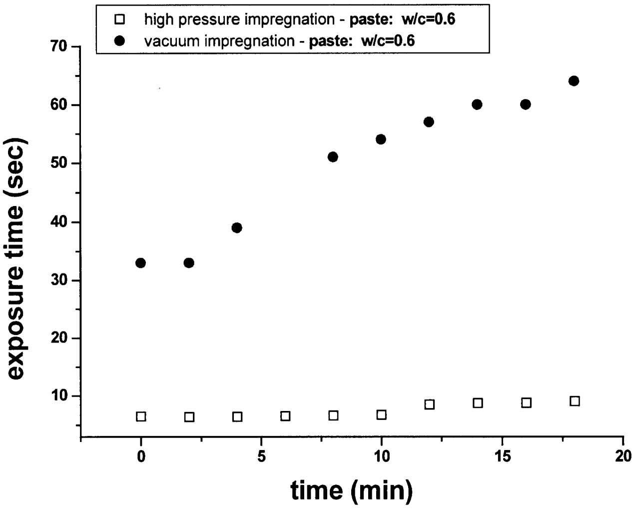

Fig. 6. Comparison of the UV fluorescence stability of high-pressure- and vacuum-impregnated samples.

vacuum impregnation, whereas the high-pressure impregnation method is significantly more efficient in filling the pores of the specimen as shown by the large fraction of the pores with the fluorescent epoxy resin (see Fig. 4 — 100 and 400 bar impregnation pressures).

3.3. Quality and stability of fluorescence: high pressure vs. vacuum impregnation

So far, discussion of the results from this study have focused on the effectiveness of two different impregnation techniques on a "macro" scale (mm to cm). However, thin-section fluorescence microscopy is a commonly adopted technique to characterize the microstructure of cement based materials [13,14] on a finer, "micro" scale (μm to mm). Fluorescence microscopy is an extremely useful means to evaluate the degree of hydration [14,15], microstructural defects (microcracking, crack patterns, debonding, permeable zones, etc.) [13], pore structure and its size distribution [13] and the interfacial transition zone (ITZ) [13]. In order to obtain reliable and reproducible results from fluorescence microscopy, it is important to have a robust impregnation procedure that results in a uniform and vast distribution of the fluorescent epoxy resin throughout the material structure. A uniform and stable intensity will enable precise quantification and identification of the aforementioned microstructural features.

The impregnation technique should yield samples of which fluorescence demonstrates a high degree of stability. This means that the intensity of the fluorescent epoxy viewed in an optical microscope under UV light should not exhibit a significant decay with time, and, in particular, during the time of observation and analysis. Fig. 6 is a plot of the exposure time required to reach a set threshold value of photons measured at different times while the sample is continuously exposed to a UV light source. The measurements are performed at the same magnification (10 ×) for a high-pressure and vacuum-impregnated sample of the same W/C — 0.6. Note that the dosage of fluorescent dye is the same for both samples. Therefore, differences in intensity can only arise from the effectiveness of the impregnation

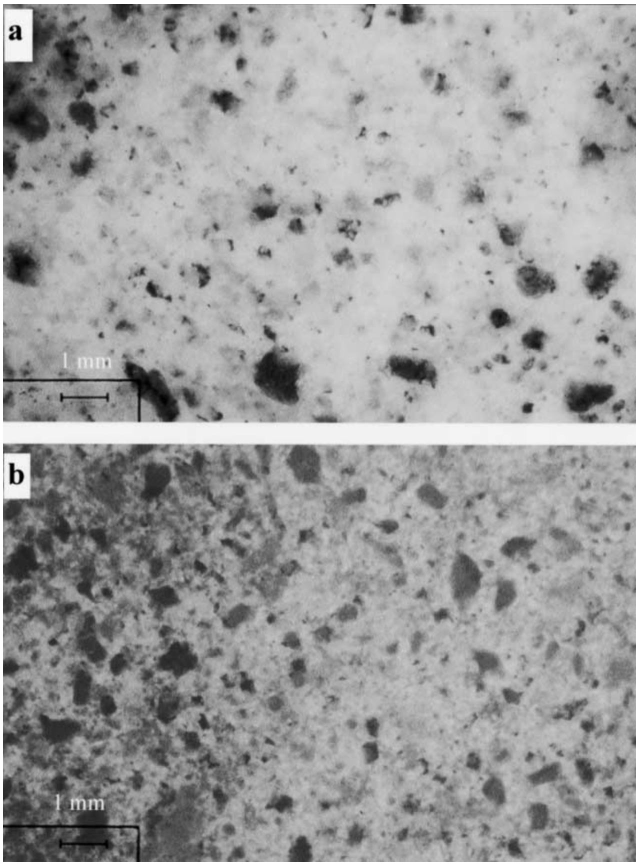

Fig. 7. Microscopic comparison of the UV fluorescence intensity in high-pressure-impregnated (a) and vacuum-impregnated (b) samples.

method. The intensity of the impregnated UV fluorescent dye is inversely related to the exposure time as explained in Section 2.5. Over a period of 18 min, one can clearly observe from Fig. 6 that the vacuum-impregnated samples have a higher exposure time, and therefore, a lower fluorescence intensity. Furthermore, the intensity of the vacuum-impregnated sample is not stable after 2 min of exposure to UV light, and decreases in a continuous fashion with the elapse of time. Whereas the high-pressure-impregnated sample shows a higher and significantly more stable intensity than the vacuum-impregnated sample. High-pressure impregnation is more effective in terms of polymer penetration into the microstructure, and this yields a more reliable and reproducible output for quantitative microstructure characterization.

The images shown in Fig. 7 support the intensity measurements given in Fig. 6. Note how the brightness of the pressure-impregnated sample (Fig. 7a) is greater than the vacuum-impregnated sample (Fig. 7b). A greater brightness is an indication of a higher content fluorescent epoxy and more effective penetration of the epoxy into the material microstructure. Thus, the denser the dye content in a region of a sample, the more stable the fluorescence over time.

4. Conclusions

Most of the cementitious samples prepared for microstructural investigation have been limited to vacuum impregnation, epoxy–solvent exchange, and low-pressure impregnation (<20 bar). This study presents an alternative, effective, and reliable method for preparing fluorescent epoxy-impregnated samples for microstructure characterization defined as high-pressure impregnation. Thus, characterization of high-pressure impregnation range is conducted on varying W/C paste (0.3, 0.5, 0.6), an EN 196 NM, and FM. From polymer loading studies, a saturation pressure (P_{sat}) is observed for the various cementitious specimens. A sectioning technique combined with the use of UV light proved to be a very useful method in characterizing the penetration profile of the polymer into cementitious materials. The absence of the penetration front is clearly visualized at the pressure corresponding to P_{sat}, confirming the observation that pores are virtually completely filled at this pressure. Close examination of the polymer loading data reveals that P_{sat} is a parameter sensitive to the material's microstructure, particularly the pore structure. In paste samples, the polymer loading at P_{sat} increases with increasing W/C. However, in mortar samples of equivalent W/C (0.5), the polymer loading behavior is dissimilar due to differences in porosity and aggregate type.

High-pressure impregnation above 20 bar proves to be an extremely effective and relatively rapid method to impregnate cementitious materials. Furthermore, examination of the stability of the fluorescence in thin-section samples indicates that cement-based materials subjected to high-pressure impregnation exhibit a greater stability and higher intensity when compared to samples prepared by conventional vacuum impregnation. The latter attribute is important for a more reliable and accurate quantitative as well as qualitative analysis of the microstructure in cement-based materials.

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