

## THE MICROSTRUCTURE OF POLYMER CEMENT MORTARS

Harald Justnes, Research Engineer (PhD) &  
Bjarte Arne Øye, Research Engineer (PhD)  
Cement and Concrete Research Institute,  
The Foundation for Scientific and Industrial  
Research, N-7034 Trondheim, NORWAY



### ABSTRACT

Polymer cement mortars (PCC) have been made by replacing a given volume of the cementitious paste with polymer and simultaneously keeping the w/c-ratio constant. PCC's with 5, 10, 15 and 20 vol% polymer were investigated by SEM after partly removing the cementitious paste by acid etching. This revealed that the polymer phase formed a continuous network if the dosage was between 5 and 10 vol%.

The influence of the film-forming ability of the polymer network formation was shown by using two polymers of equal chemical character, but with minimum film-forming temperatures (MFT) below and above the curing temperature.

The crack bridging ability of the polymer phase in PCC was revealed on fracture surfaces by SEM, explaining the generally improved flexural strength by latex based PCC's. The polymer phase was confirmed by EDAX-analysis. The latter experiment was performed also for an epoxy modified PCC, showing the polymer phase as larger, irregular shaped clusters. This observation was utilized to explain why an epoxy based PCC maintain its improved flexural strength regardless of the moisture content (unlike latex based).

Key-words: Polymer Cement Mortar, PCC, Latex, Epoxy, Micro-structure, Minimum film-forming temperature.

### 1. INTRODUCTION

The improved mechanical and durability properties of PCC vs ordinary cement concrete (CC) /1-5/ have triggered a curiosity for revealing how the polymer phase works together with the cementitious phase in such a concrete-polymer composite. A theoretical model leading to the formation of an interweaved polymer network was put forward by Ohama /6/. The model is discussed later in the light of the present observations. Chandra and Flodin /7/ made a literature survey over the microstructure of PCC, discussing the purely physical model with the coalescence of polymer spheres to polymer films against a chemical model with possible complex formation

between functional groups in the polymer and the cementitious minerals. The latter effect is sought utilized by Justnes and Dennington /1/.

## 2. EXPERIMENTAL

The preparation of the PCC's based on latex /4/ and epoxy /5/ is thoroughly presented in the quoted references. All PCC's in use were older than 3 months.

Pieces of PCC with a typical dimension of 2 cm were broken loose by blows from a hammer. The bits used to image the fracture surface were used as such, while those which should reveal the polymer network were etched with an 1 M hydrochloric acid (HCl) solution for a few minutes, washed and dried. All samples were coated by a layer of carbon or gold (those who were subjected to carbon analyses) prior to the scanning electron microscope (SEM) investigation.

The present investigation was mainly carried out with a Jeol JSM-840 SEM, creating micrographs by secondary electrons and using back scattered electrons (BSE) image at an accelerating voltage of 3.5 to 20 kV to find the epoxy phase in PCC (fig. 8). The microscope was equipped with a Link Analytical energy dispersive system for element analyses (EDXA). A Jeol-T200 SEM utilizing secondary electrons at 25kV was also used in this study. The latter microscope was not fitted with an EDXA.

## 3. RESULTS

In order to find out at which polymer dosage a continuous network was formed when the w/c-ratio was 0.55, samples with 5, 10 and 15 vol% polymer of the total binder content (cement, water and polymer) added as latex was etched and inspected by SEM. The latex was based on a terpolymer containing n-butylacrylate (BA), methylmetacrylate (MMA) and a functional monomer (A2) /1/. The photographs at a 100X magnification are shown in figure 1, 2 and 3, respectively. It can be seen that the polymer phase get to be continuous at a dosage between 5 and 10 vol%. Indication of the same fact could be observed during the acid etching, since the piece with 5 vol% polymer tended to disintegrate, while both samples with 10 and 15 vol% polymer stucked together. Figure 4 is a close up (400X) of the 15 vol% sample shown in figure 3.

While the PCC's in figure 1-4 is based on an acrylate with minimum film-forming temperature (MFT) of 12 °C, figure 5 shows the etched surface of a PCC based on an acrylate based on the same three monomers, but with a composition leading to a MFT of 28 °C. The latter temperature is slightly above the curing temperature of 23°C, and it may look as if the polymer particles from the latex have not been able to "melt" properly together (fig. 5).

It has been claimed in the literature several times that polymer supplied as latex is able to bridge microcracks in PCC, and thereby explain the increased flexural strength. This effect is shown

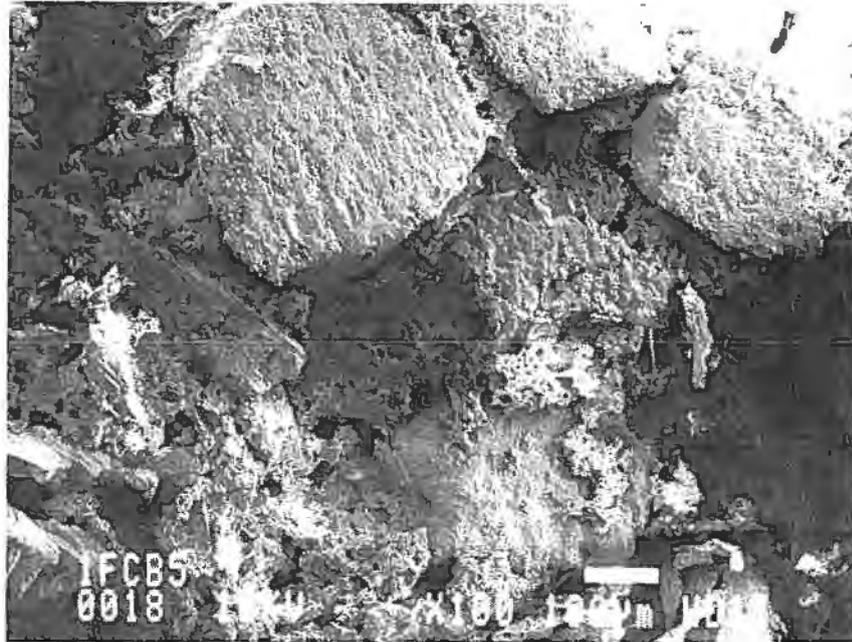


Fig 1. Etched surface of a PCC with 5 vol% acrylate (100 X SEM)

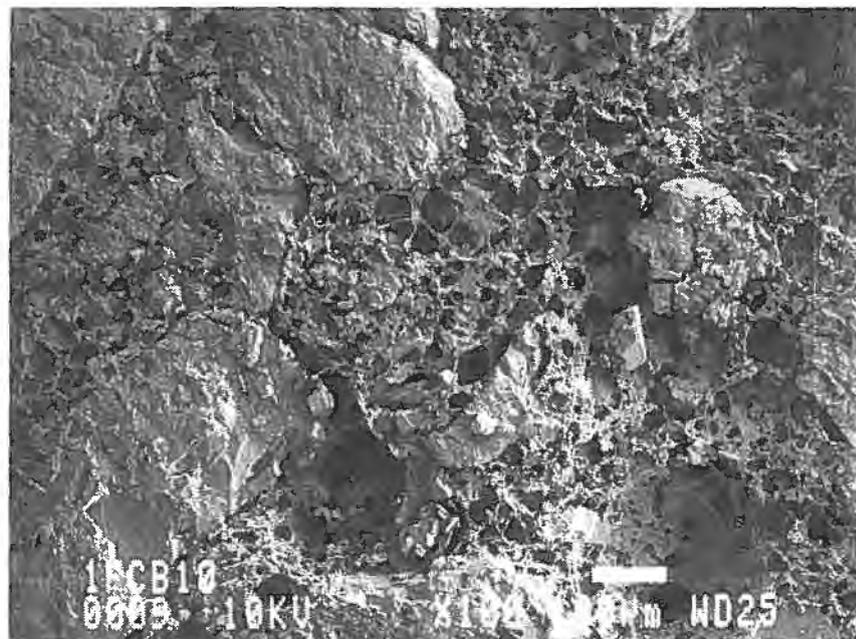


Fig 2. Etched surface of a PCC with 10 vol% acrylate (100X SEM)

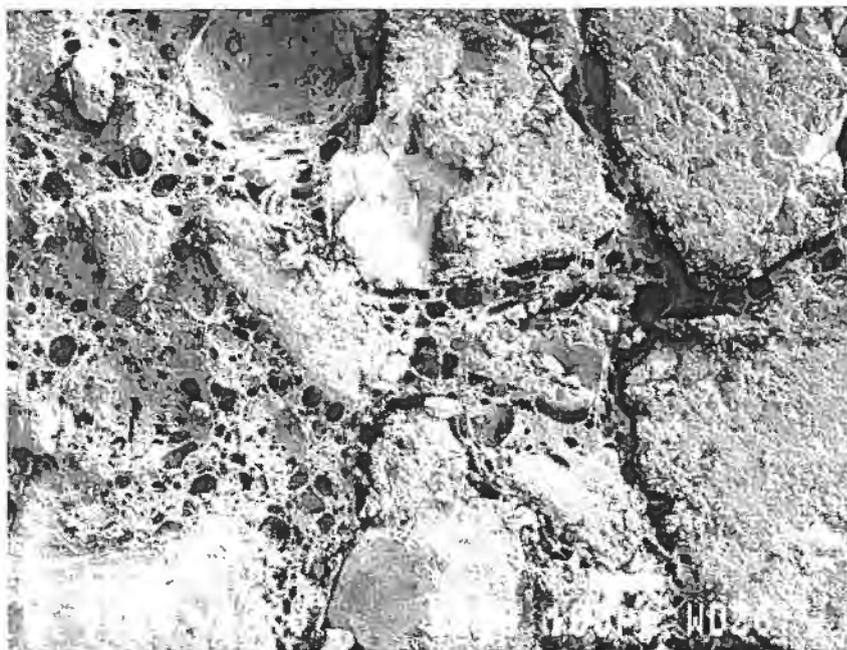


Fig 3. Etched surface of PCC with 15 vol% acrylate (100X SEM)

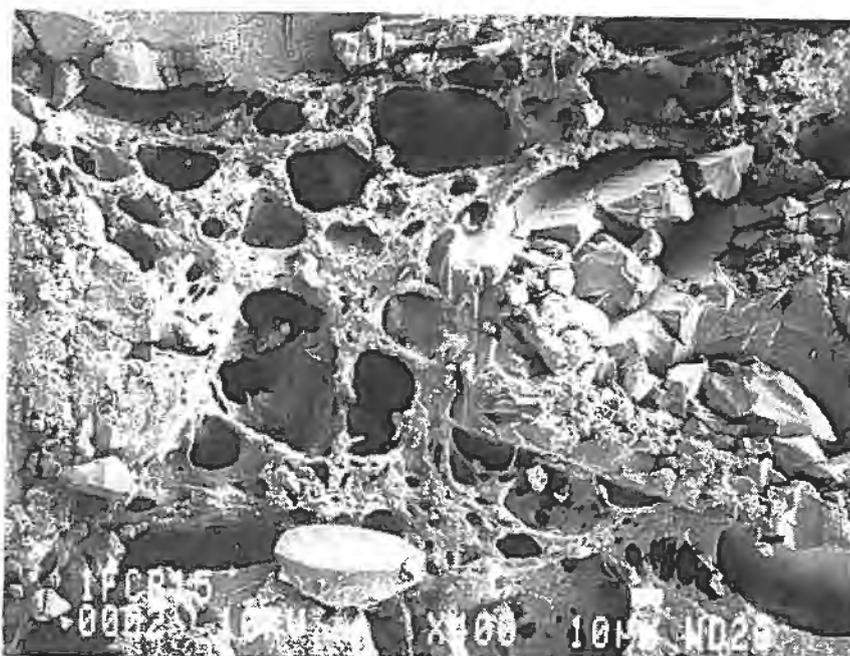


Fig 4. Etched surface of PCC with 15 vol% acrylate (400X SEM)

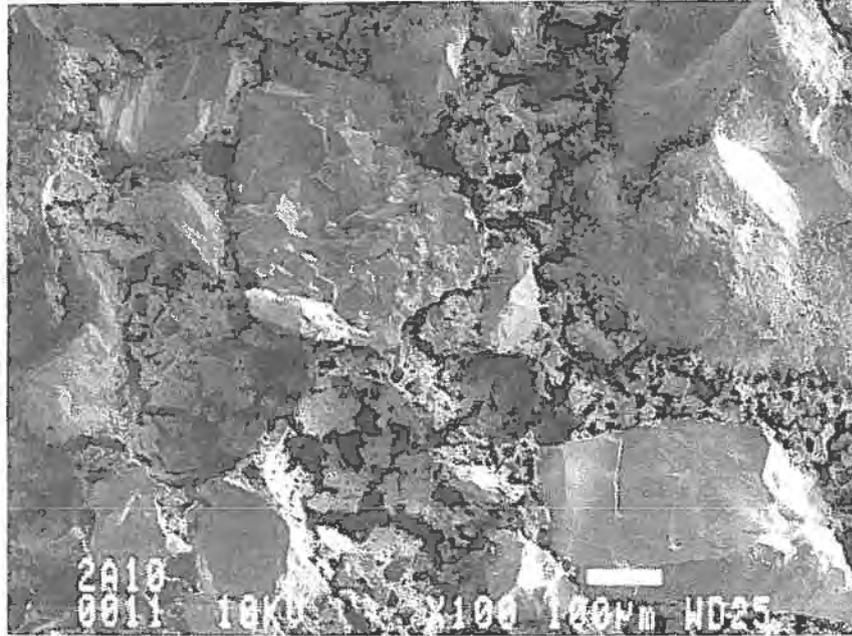


Fig 5. Etched surface of PCC with 10 vol% acrylate with a minimum film-forming temperature slightly higher than the curing temperature (100X SEM).



Fig 6. Fracture surface of a PCC with 10 vol% SBR showing the crack bridging ability of the polymer (12000X SEM)

in figure 6 for a PCC based on SBR and in figure 7 for a PCC based on PVAc/PE/PVC. In the latter case, it has been confirmed that the observed threadlike structure over the crack consist of polymer by detecting chlorine from the PVC by EDAX-analysis. Other elements (like calcium) are also detected since the volume analyzed is about  $1 \text{ } (\mu\text{m})^3$ .

The epoxy based PCC was made by blending the epoxy and hardener, and then add this to the cementitious mortar. The whole mix was then thoroughly mixed by an electrical drill with an attached propeller. However, figure 8 reveals that the epoxy is enriched in clusters appearing as darker areas in the BSE image obtained by SEM. In a BSE image, it is known that structures consisting of lighter (e.g. hydrogen and carbon) elements appear darker than areas of heavier elements (e.g. calcium and iron). It was confirmed by EDAX-analysis that the darker area was enriched in carbon, while the lighter areas contained very little carbon (calcite filler).

#### 4. DISCUSSION

The principle of polymer network formation in a latex based PCC, as proposed by Ohama /6/, is slightly modified by the authors. The simplified model is depicted in figure 9 and may be described as follows: Immediately after mixing, the different phases like aggregate, unhydrated cement grains and polymer particles are evenly dispersed in water. The formation of a polymer network proceeds then in three steps: First step: The polymer particles deposit partially on unhydrated and partly hydrated cement grains. Second step: With consumption of water due to the development of cement gel structure, the polymer particles ( $0.1 \text{ } \mu\text{m}$  in size) are gradually confined in the capillary pores. As the cement hydration proceeds further and the capillary water is reduced, the polymer particles flocculate to form a continuous close-packed layer of polymer particles on the surfaces of the cement gel/unhydrated cement particle mixture. At this stage, the cementitious binder has already established its continuous interconnections. Third step: Ultimately, with water withdrawal by cement hydration, the close-packed polymer particles on the cement hydrates coalesce into continuous films or membranes, and the films or membranes form together with the cement hydrates a monolithic network. Thus, the continuous networks of both polymer film and cement hydrates are interweaved. However, in the last step it is assumed that the minimum film-forming temperature (MFT) of the polymer is lower than the curing temperature.

The SEM-photographs of the etched surfaces of PCC based on an acrylate with a MFT of  $12^\circ\text{C}$  in figures 1-4, reveal that the above model is basically correct, and that a dosage of between 5-10 vol% polymer is necessary for the network to be continuous at a w/c-ratio of 0.55. Note that according to the model, the necessary

dosage of polymer for a continuous network may be lower at lower w/c-ratios. In the upper left corner of figure 3, it seems that the entrained air bubble is enriched with polymer on the surface. Thus, a defoaming agent should be employed in order to not waste

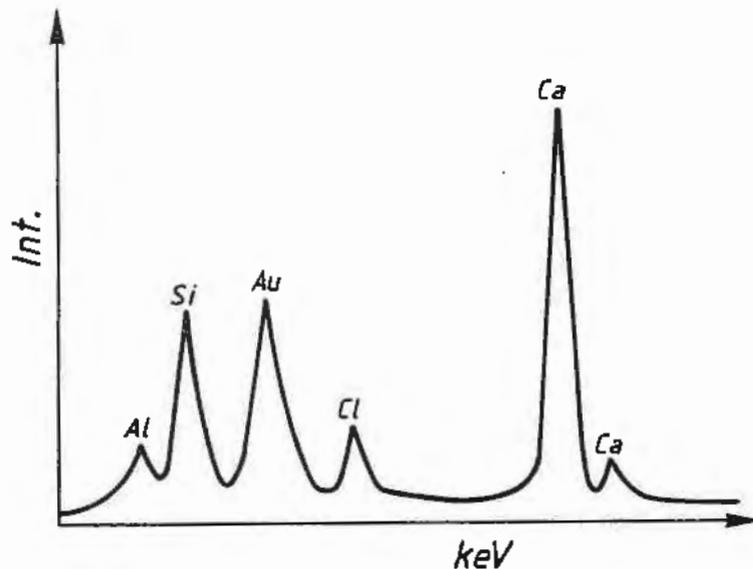


Fig 7. The fracture surface of PCC with 10 vol% PVAc/PE/PVC polymer revealing multiple threads over a crack (16000X SEM). The EDAX analysis in the lower part of the figure is of analogous thread formation showing chlorine signals (from PVC).

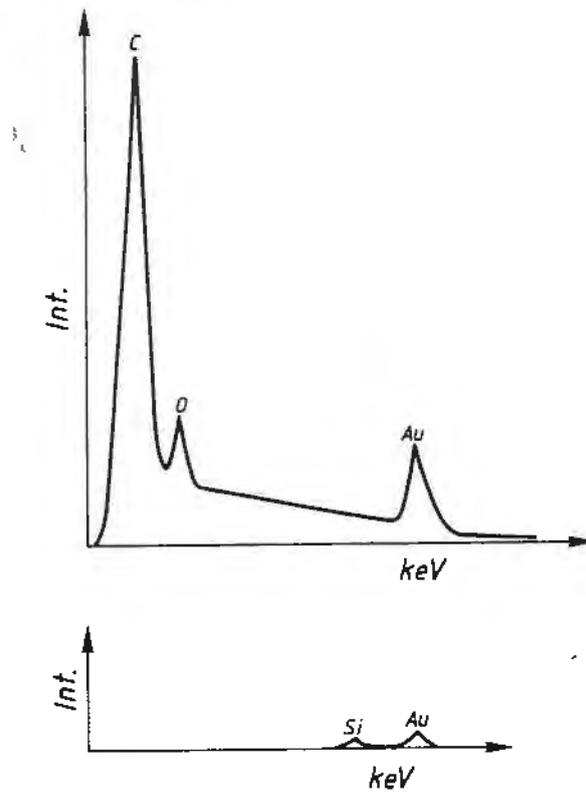


Fig 8. BSE picture (270X SEM) of the fracture surface of PCC with 10 vol% EPOXY F0, with element analyses recorded in point X1 (middle) and X2 (bottom). The carbon peak is strong in X1 and practical lacking in X2, showing that the epoxy gathers in clusters appearing as darker areas.

expensive polymer. Justnes et al /3/ have shown that for PCC's with the same dosage of polymer, but with different air content, the one with the lowest amount of entrained air perform best in the durability tests (e.g. chloride ingress).

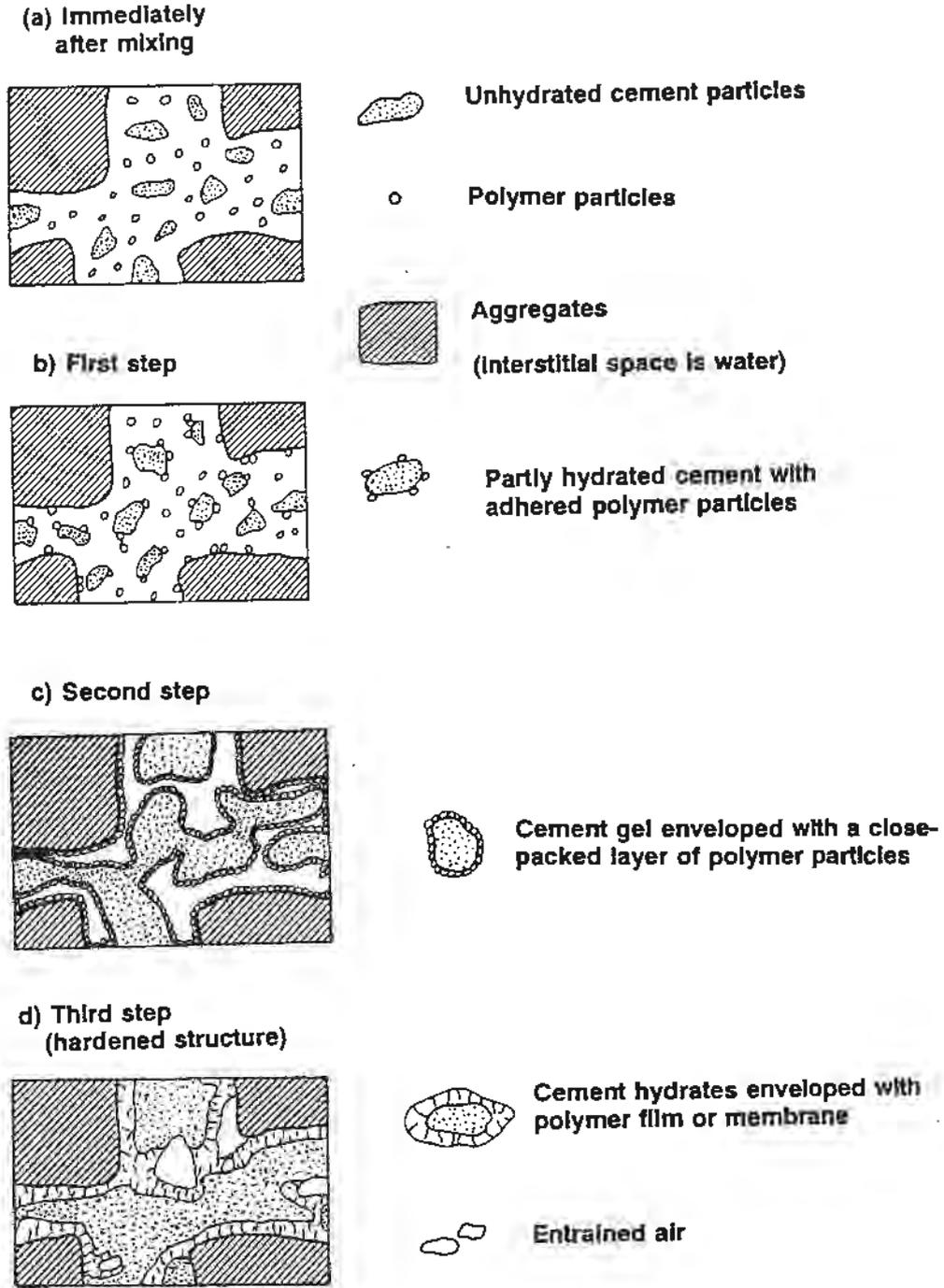


Fig 9. Simplified model of the formation of a polymer-cement comatrix in a latex based PCC according to Ohama /6/

The importance of a MFT lower than the curing temperature, is shown in figure 5. This acrylate is based on the same monomers as the acrylate in figures 1-4, but the MFT is now 28°C. Apparently, the polymer particles have not been soft enough to coalesce properly. This will in turn lead to inferior flexural strength and durability properties for the PCC.

Since the acrylate with functional monomers also seems to coalesce to a continuous polymer film (fig 1-5), any complex formation between functional groups in the polymer and cementitious minerals will only take place in the interface between the polymer phase and the mineral phases.

The crack bridging ability of SBR and PVAc/PE/PVC polymers revealed in figure 6 and 7, respectively, may explain the increased flexural strength and fracture energy observed /2/ for the resulting PCC's. The elastical nature of these polymers may also help to distribute stresses in the matrix, and thereby reduce crack growth. This may in turn explain the generally increased durability of PCC vs CC (in addition to hydrophobizing effects /1/, /5/).

The distribution of epoxy resin in the resulting PCC, as shown in figure 8, leads to the conclusion that the hardened epoxy may be looked upon as highly irregular lumps, sheets or fibres with a propagation freedom in three dimensions. This give "fibres" a opportunity of interlocking in the cementitious paste. In addition, epoxy exhibits in general a good adhesion towards hardened concrete. The result is well documented /5/; an improved flexural strength. A surprising result /5/ was that the PCC based on epoxy, unlike PCC based on for instance SBR-latex, retained the improvement in flexural strength even when it was wet (submersed 7 days in water). This observation was made by curing the PCC according to three different schedules; I: 28 days at 50% R.H. and 20°C ("dry"), II: 14 days at 50% R.H., 7 days submersed in water and 7 days at 50 % R.H. ("dry-wet-dry") and III: 21 days at 50 % R.H. and 7 days submersed in water ("dry-wet"). The result is depicted in figure 9 as flexural strength relative to the flexural strength for plain mortar at w/c = 0.40 after curing scheme I. Eventhough the absolute level of the flexural strength do vary with the air content as indicated, it is evident that the epoxy based PCC retain its flexural strength when wet (curing scheme III) compared with the PCC based on 10 % SBR latex. Note also the dramatic loss of flexural strength for the reference mortar after curing scheme II, which probably is due to microcracking in the dry-wet-dry cycling. The effect is not as pronounced for either of the PCC's. The preceding observation may be explained by the fact that the epoxy resin cure "in situ" to a hard substance and contain no surfactants, while the latex is a "ready cured", soft polymer dispersed in water by emulsifiers. When the PCC is rewetted after drying, these emulsifiers or surfactants may possibly partly reemulsify the polymer, partly perforate the film or entrain water and thereby weaken the polymer film. These possibilities are excluded in the case of epoxy.

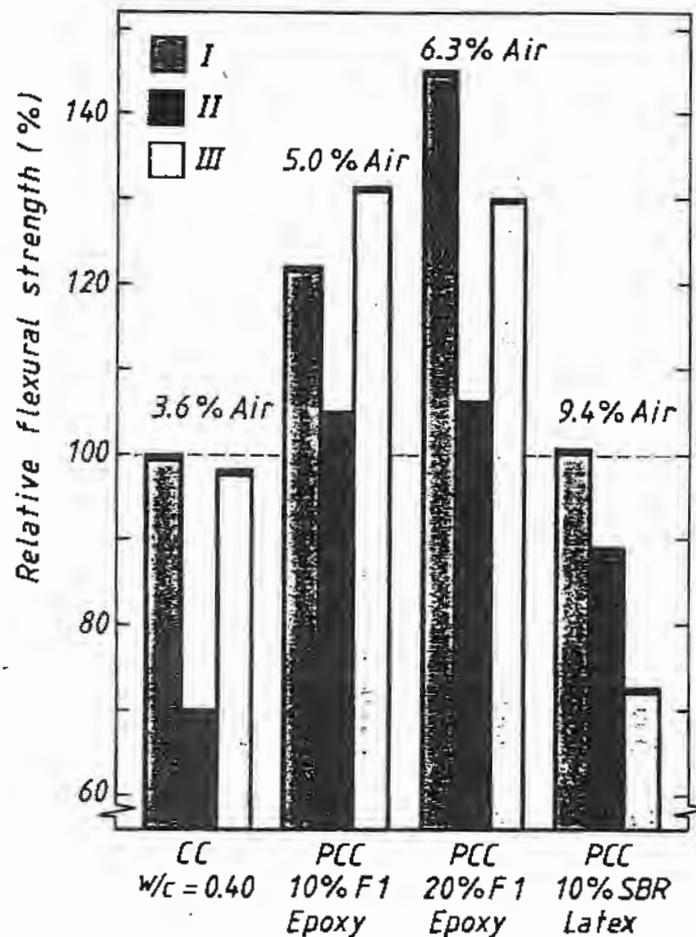


Fig 10 The relative flexural strength of epoxy based PCC compared with cement mortar and PCC based on SBR latex, respectively.

The epoxy based PCC had also a strongly reduced capillary suction /5/, suggesting that some of the epoxy may be finely distributed in the capillary pores as well or that the capillaries simply were segmented due to clusters of epoxy.

## 5. CONCLUSION

Evidences have been found that support a model which leads to the formation of interpenetrating polymer network in polymer cement mortar/concrete (PCC) based on latices.

The importance of the polymer to have a minimum film-forming temperature (MFT) below the curing temperature, in order to form a proper film, has been visualized.

The crack bridging ability of polymers in latex based PCC has been verified, explaining the increased flexural strength and fracture energies observed for these materials.

It is important that the latex entrain as little air as possible (may be adjusted by a defoaming agent) in order to obtain a cost/-efficient material (lesser amounts of expensive polymer is needed to obtain similar effects).

The microstructure of PCC based on a epoxy resin has been revealed, showing irregular clusters of epoxy in the cement paste. This observation is used to explain why the epoxy based PCC exhibit an improvement in flexural strength insensitive to moisture, unlike PCC based on for instance SBR-latex.

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