TECHLINE2
FOR THE CONSTRUCTION INDUSTRY

Effect of Performance Additives on the Microstructure of Cement Mortars

ABSTRACT
Performance additives like cellulose ethers and redispersible polymer powders determine to a large extend the application properties of cement mortars. We investigated the impact of different cellulose ethers and redispersibles polymer powders on the microstructure of a cement based tile adhesive.

Workability, adhesive strength and open time are influenced by the type and amount of pores in the mortar system. The characterization of the pores was done by mercury intrusion porosimetry (MIP) which determined the accessible pore volume and the pore size distribution of the cured adhesives. We could distinguish between air pores, capillary pores and gel pores which all have different effects on the workability and physical properties of the cement based mortar.

With cryo-transver (CT) and thin cut techniques and subsequent scanning electron microscopy (SEM) we developed a deeper understanding of the air pore distribution in a real application system. The film formation kinetics of the redispersed polymer powder could be correlated with application properties. This study was based on a cooperation of Dow Construction Chemicals with the Fraunhofer Institute for Applied Polymer Research in Golm.

INTRODUCTION
Redispersible polymer powders (RDP) and cellulose ethers (CE) are additives which control to a large extend the properties of cement based tile adhesives (CBTA) and other cementitious mortars. Wet mortar properties like density, workability, rheology and open time can be adjusted to the required level. RDP's have a strong influence on the physical properties of the set mortar like adhesive strength after various ageing conditions and flexibility. The film formation kinetics and the location of the redispersed polymer in the cementitious mortar are important factors for strength development and flexibility. In addition to their role as water retention and rheology additive CE help to disperse the polymer powder in the mortar. Scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) enable a microscopic view into the structure of a CBTA in detail and help to better understand the role of these two important performance additives.

TEST METHODS AND MATERIALS

Scanning Electron Microscopy (SEM)

SEM was used to study the morphology and pore structures of the CBTA-samples. The SEM-images were taken by a JSEM 6330F (Jeol, Japan) at an acceleration voltage of 5 kV. Cross sections were prepared by fracturing the CBTA-samples in liquid nitrogen. Both open and closed air pores and also capillary pores down to a diameter of 10 nm can be detected by this method.

Cryo-preparation of mortar samples makes it possible to study the polymer film formation at very early stages. Different to an environmental SEM, a droplet or a small sample with a diameter of about 6 mm is instantly frozen in liquid nitrogen. After fracturing at – 196 °C the sample was heated to -75 °C to allow sublimating ice from the surface of the cross section within 10 min to a depth of about 500 µm, i.e. to empty water (ice) from air pores completely.

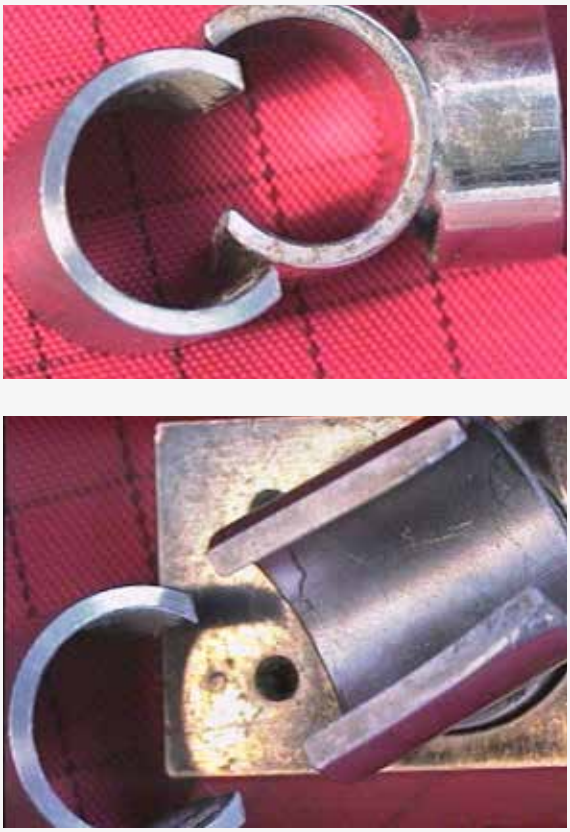

Figure 1: Sample mould for SEM investigation

Mercury Intrusion Porosimetry

Generally, mercury intrusion is a suitable method for the characterization of open and accessible pores of various sizes in cementitious mortars. This method is primarily used to determine the specific volume and the specific surface of the pores and to calculate the porosity and the bulk density of the CBTA-samples. Prior to Hg-intrusion the samples with a maximum volume of 2 cm3 were thoroughly dried and conditioned for 3 h to ensure complete removal of moisture. **Table 1** gives an overview of the of pore types in cementitious mortar.

PORE TYPE	PORE SIZE
Gel- or shrinked pores	1 – 10 nm
Capillary pores	10 – 100.000 nm
Air pores	> 10.000 nm

Table 1: Pore classification[1]

The parameters of the pore size distribution were calculated from the curve of the cumulative pore volume from Washborn's equation[2] for open pores, assuming cylindrical pore geometry. Generally, air pores contribute mainly to the specific volume and therefore to the density of the CBTA-samples, while capillary pores contribute primarily to the specific pore surface.

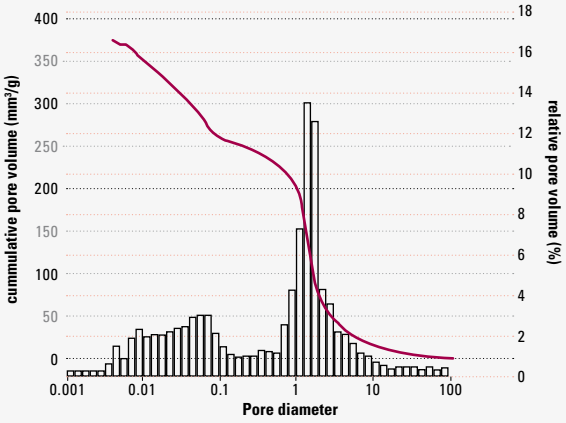

Figure 2: MIP- Pore distribution

Mortar Preparation

Our investigations were based on three different cement based tile adhesives, containing combinations of various additives. We used two redispersible polymer powders. RDP 1 is a vinyl acetate/ethylene copolymer and RDP 2 contains in addition to vinylacetate and ethylene also vinyl versatate (VeoVa) as monomer (**Table 2**). Both polymer powders have a minimum film formation temperature (MMFT) of 3°C.

	COMPOSITION	MFFT [°C]
RDP 1	VAc/E-Coploymer	3
RDP 2	VAc/E-VeoVa	3

Table 2: RDP composition and Minimum Film Forming Temperature (MFFT)

The cellulose ethers used in this report were hydroxypropyl methyl cellulose and hydroxyethyl methyl cellulose (HPMC and HEMC) of the same viscosity range but with different substitution levels. Both cellulose ethers had a methyl degree of substitution (DS) of 1.80. The hydroxypropyl molecular substitution level (MS) of the HPMC sample was 0.28. The hydroxyethyl MS of the HEMC product was much lower and had a value of 0.17.

	DS	MS	VISCOSITY (MPA·S)*
HPMC	1.80	0.28	40000
HEMC	1.80	0.17	40000

Table 3: CE properties (*) Viscosity level is based on: 2% solution, 20°C, D= 2.55 s^{-1} (Rotovisco))

All CBTA samples were mixed and applied according to EN 12004 for CBTA. **Table 4** shows the mortar formulations which we have used for our investigations.

	DIM	G1	G2	G3
CEMENT (CEM I 52.5 R)	%	30.0	30.0	30.0
SAND F 36	%	67.5	67.5	67.5
RDP 1	%	2.5	–	2.5
RDP 2	%	–	2.5	–
HPMC	%	0.5	0.5	–
HEMC	%	–	–	0.5
WATER	%	0.28	0.28	0.28
WET MORTAR DENSITY	kg/l	1.46	1.47	1.44

Table 4: CBTA formulations

The wet mortar densities of formulations G1 and G2 are very similar. Formulation G3, however, entrains slightly more air. The combination of RDP 1 with HEMC gives the lowest density of 1.44 kg/l.

Figure 3 shows the adhesion strength after normal storage, water immersion and 20 min. open time. All values are within the range of the accuracy of the experiments, with one exception. RDP 1 in combination with HEMC shows the lowest adhesion strength which could be the effect of the lower fresh mortar density.

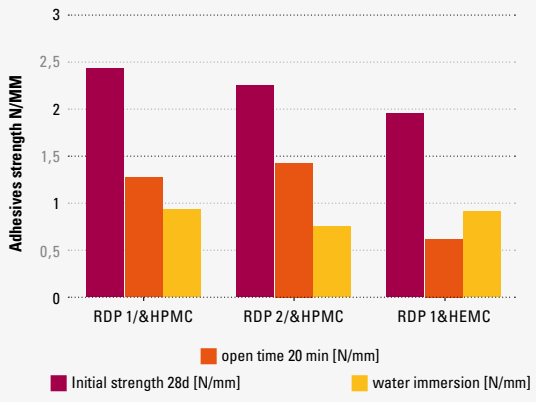

Figure 3: adhesives strength results according EN 1346/1348

RESULTS AND DISCUSSION

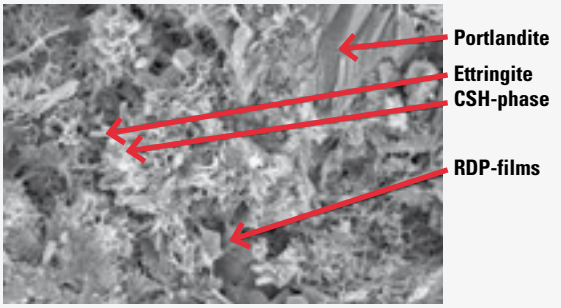

Figure 4: dry fractured cross section, setting time 28 days

Figure 4 illustrates the microstructure of cement based tile adhesives after 28 days of setting and documents the vast variety of crystalline and amorphous structures present in a cured mortar sample. Tabular-shape Portlandite crystals, needle-shaped Ettringite crystals and leaf-shaped Calcium-Silicate-Hydrate-phases are well visible[3]. The latex films between Ettringite, Portlandite and CSH–phases are an important element of the microstructure of a cementitious mortar and improve the flexibility between the brittle crystal structures.

MICROSTRUCTURE – MIP ANALYSIS

Mercury intrusion porosimetry is a widely used technique to determine the pore size distribution in cementitious mortars[4]. However, this method is has its limitations based on the simplified assumption of regular pore geometry and reduced connectivity of the accessible pores. In our experiments we have found acceptable reproducibility of the pore size distribution of a given sample. The MIP data have been used as a relative measure. Their absolute values have to be considered with care.

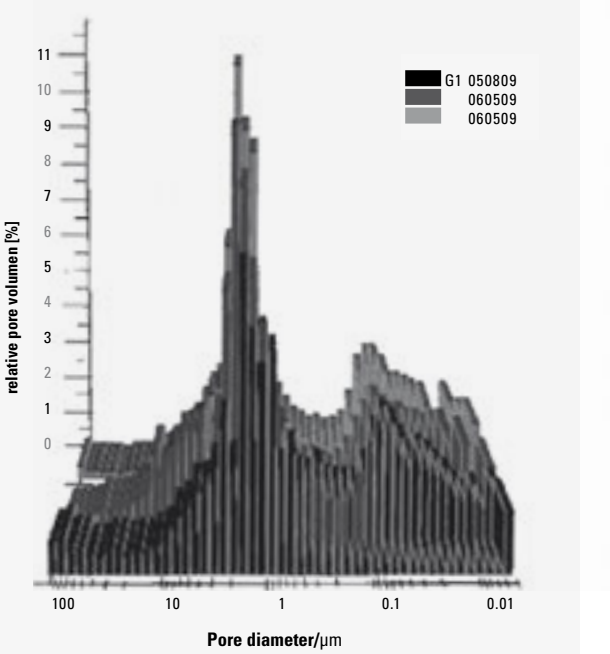

Figure 5: Reproducibility of MIP measurements on mortar sample G1

Figure 5 shows the pore size distributions of three different measurements of mortar sample G1. Two distinct peaks at about 1.5 µm and 0.08 µm could be detected. The biggest portion of pore volume in the dried mortar samples consists of small capillary pores. The pore volume contribution of air pores (diameter > 6 µm) is relatively small.

Impact of Cellulose Ether on the Pore Formation

The effect of CE on the pores can be demonstrated when looking at the MIP data of mortars containing different CE's. **Figure 6** illustrates the pore size distributions of the three mortar samples described in **Table 4**.

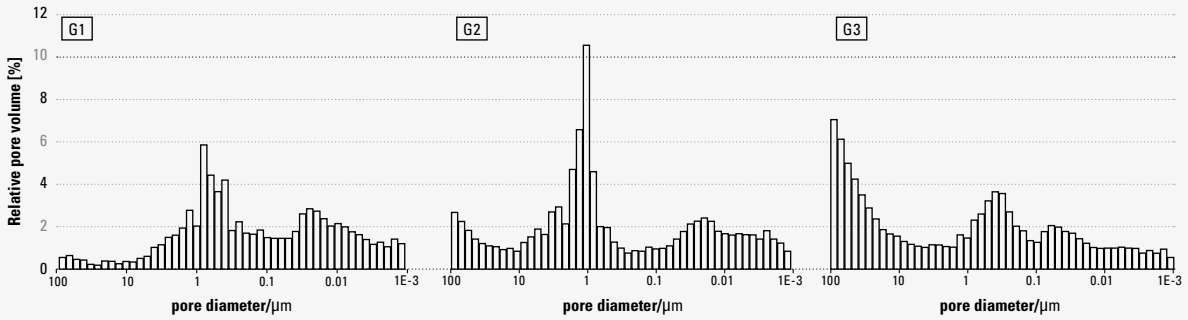

Figure 6: MIP – Pore size distribution in mortar

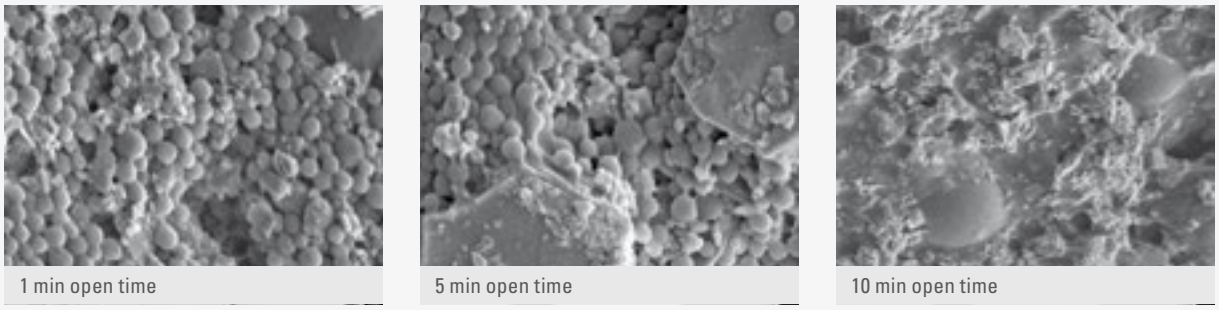

Figure 7: Film formation of RDP 1 after different open times

Sample G1 and G2 were prepared with the same HPMC but different RDP chemistries. The MIP result shows that the capillary pore size shows the maxima at 1.5 µm and 0.08 µm in both cases independent from the redispersible polymer powder. Sample G3 contains the same RDP as sample G1 but with HEMC as thickener. A significant reduction of the maximum pore diameter to ~ 0.8µm could be detected which can be the result of the surface activity of the CE. This is mainly controlled by the content and chemistry of the hydroxyalkyl substituent. The fresh mortar densities of sample G1 and G2 were quite similar. The HEMC based mortar had slightly more air entrained causing less fresh mortar density (see **Table 4**).

The results of the MIP experiments show that CE have a significant impact on the pore structure in CBTA. The RDP's used in this set of experiments did not seem to influence the pore size distribution.

MICROSTRUCTURE ANALYSIS WITH SEM

Time Dependent Film Formation in the Cement Matrix

Mortar samples were taken immediately after mixing and prepared accordingly to have the surface investigated in the scanning electron microscope.

Figure 7 illustrates the film formation on the surface of a mortar sample within the first 10 minutes after mixing. After water addition to the mortar the latex powder particle starts to redisperse. The SEM pictures after 1 min open time shows that they disintegrate into the initial latex particles with a size in the range of 1 µm and accumulate on the surface. The SEM picture after 5 minutes illustrates the beginning of the film formation. The particle just starts to melt together to form a compact latex film. After 10 minutes the mortar surface is completely covered by the latex film. The first CSH-crystals grow through the film and start to develop their typical leaf shaped morphology.

The View into an Open Pore – Location of RDP in pores

Our preparation techniques enabled us to have a view into an open air pore of a cementitious mortar. Figure 8 shows an open mortar pore after 30 minutes and 5 hours of setting of a vertical cross section. After 30 min setting some of the initial latex particles are well intact and in some other areas of the air pore the first film formation has just started.

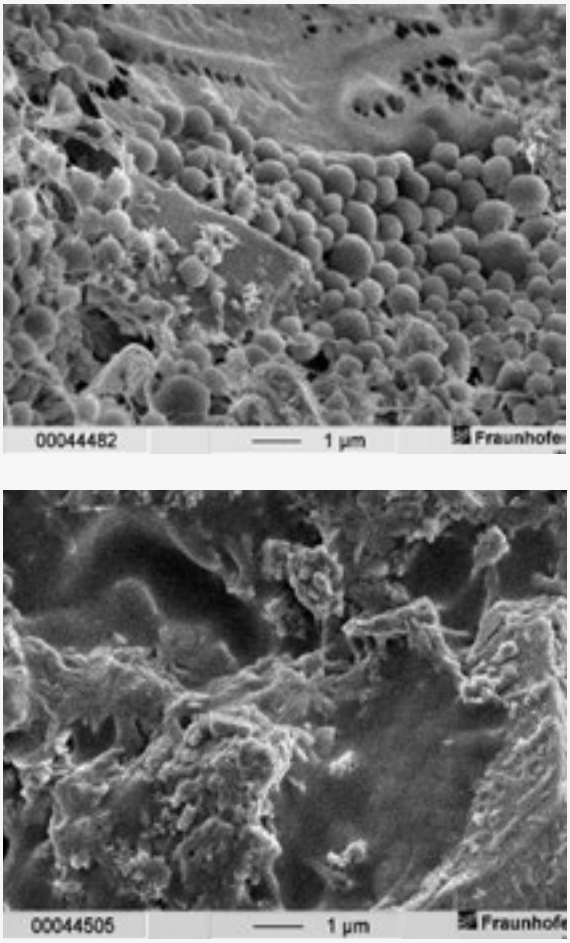

Figure 8: Opened pore – Vertical cross section, 30 minutes and 5 hours setting time

After 5 hours setting time the pore surface is complete covered with a latex film. The RDP particle structure is not visible anymore.

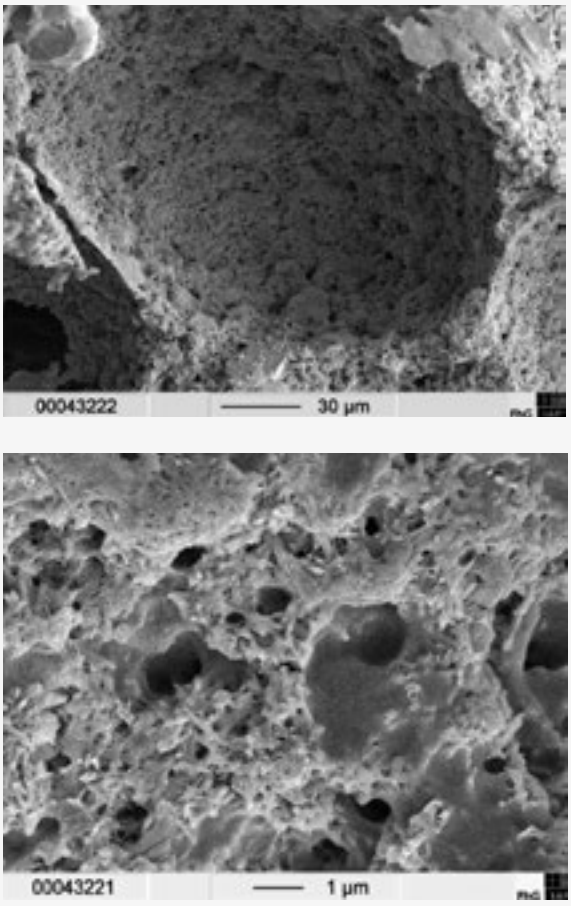

Figure 9: The view into an open air pore, after 28 days of setting time

The SEM photograph of an air pore of a mortar which has cured for 28 days illustrates its complex structure. The growing crystals as a result of the cement hydration reaction have thoroughly penetrated the latex film and cover completely the interior side of the air pore.

Re-wetting of Setting Mortar

Cement based tile adhesives which contain RDP as additional binder show strong adhesion after normal curing. When exposed to water ageing the bond strength is drastically reduced (**Figure 3**). The strength of the mortar is reduced to the contribution of cementitious structure[5].

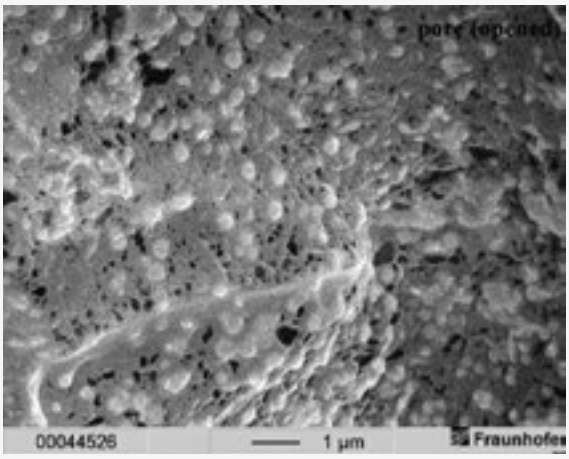

Figure 10: Mortar sample after 28 days of setting, re-wetted in water for 24 hours

An interesting observation could be noticed when we investigated the fractured surface of a cured CBTA sample which was re-wetted in water for 24 hours. After the re-wetting the sample was frozen in liquid nitrogen and prepared for the SEM analysis. **Figure 10** illustrates how the latex film changed after water immersion compared to the dry film (**Figure 8**). The initial polymer particles of the latex have reappeared but they are smaller compared to the initial stage before coalescence. A holey polymer net connects these particles. The polymer film has substantially lost integrity and it is not a surprise that it cannot contribute to the overall mortar strength anymore.

CONCLUSIONS

In our technical investigation we could demonstrate the role of RDP and CE in a cementitious mortar. Cellulose ethers are used as thickening and water retention additives. RDP's are needed to improve the adhesive strength and the flexibility. MIP, SEM and cryo-technique enable us to build up an understanding of the position and the role of CE and RDP in the cementitious matrix.

It was shown (**figure 6**) that the cellulose ethers have an impact on the pore size distribution of the finished mortar. The major pore volume is composed of capillary pore having diameters in the range of 0.01 µm – 6 µm. The HPMC sample in our investigation caused a pore size maximum of 1.5 µm, where as the HEMC based formulation resulted in capillary pores only half the size (0.8 µm).

The film formation of the redispersed latex could be well followed with SEM photographs taken at various stages of the setting process (**figure 7**). After redispersion a continuous polymer film within the cementitious matrix is built as the water evaporates. The cement hydration products penetrate this film upon further curing. When exposed to water immersion the polymer film partly dissolves leaving parts of the initial spherical polymer particles behind (**figure 10**). The redispersed latex particles have a size in the range of 0.5 µm – 1.0 µm. The capillary pores of the mortar structure have about the same size. In order to achieve maximum bond strength the polymer film and the inorganic mortar matrix need to be well interpenetrated. The latex particle should be ideally smaller than the capillary pore in order to dovetail both materials. In case of the HEMC based mortar we measured by MIP technique a pore size of about 0.8 µm, which is smaller compared to the HPMC based mortar (1.5 µm). In the latter case the latex particle can better fill out the capillary pores and achieve a more efficient penetration of the polymer film in the cementitious matrix. This effect should also result in higher strength properties (**figure 3**). The fact that we measured higher adhesive strength of the HPMC based mortars would support this mechanism. These mortars, however, had slightly higher fresh mortar densities, which also would increase strength properties to some extend. In our series of experiments both effects probably contribute to improved adhesion of the HPMC based mortars.

Further work is going on to fully understand the role of capillary pores in the mortar structure and how it can help to maximize strength properties of RDP containing cement based tile adhesives.

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