Pore structure of mortars with cellulose ether additions – Mercury intrusion porosimetry study

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Mateusz Wyrzykowski [a,b,*], René Kiesewetter [c], Josef Kaufmann [a], Robert Baumann [c], Pietro Lura [a,d]

[a] Empa, Swiss Federal Laboratories for Materials Science and Technology, Concrete/Construction Chemistry Laboratory, Switzerland
[b] Department of Building Physics and Building Materials, Lodz University of Technology, Poland
[c] DOW Construction Chemicals, Dow Wolff Cellulosics GmbH, Germany
[d] Institute for Building Materials (IfB), ETH Zurich, Switzerland

ABSTRACT

In this study, multi-cycle mercury intrusion porosimetry (MIP) was employed to study the pore structure of model tile adhesive mortars containing different types (Methyl Cellulose, Hydroxyethyl- and Hydroxy-propyl-Methyl Cellulose) and different dosages (0.3%, 0.8%) of cellulose ethers (CE). The two cycles of mercury intrusion and extrusion allowed resolving not only the total porosity of the mortar, but also the interconnected porosity of the matrix. Different application scenarios were tested: application on a substrate with no water absorption (plastic mold), on a moderately absorbing substrate (cement–fiber board) and on a substrate with high absorption (concrete slabs). These conditions allowed for determining the influence of different moisture regimes on the pore structure of the mortars. Finally, tensile adhesion strength tests with different open times were performed. It was observed that the addition of CE did not considerably affect the capillary and gel pores of the matrix. At the same time, it led to a substantial increase of the total porosity due to the entrainment of air, with slightly increasing size of entrained air voids at higher CE addition rates. A very pronounced coarsening of the porosity could be observed when mortars where applied on a substrate with high water absorption. An improvement in tensile adhesion strength respect to the reference mortar was observed thanks to CE addition, in particular for longer open times.

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1. Introduction

1.1. Use of CE in mortars

Cellulose ethers (CE) are used in dry mortars (e.g. tile adhesives, renders) as thickening and water retaining agents. Consequently they influence the properties of the wet, but also of the hardened mortar [1–5]. Due to accumulation of CE at the air-void interfaces, air voids are stabilized in a fresh mixture [6]. This process, also called air entrainment, leads to the formation of a system of stable air voids in hardened mortars, ranging from a couple of micrometers to hundreds of micrometers in diameter [5]. Air voids may occupy up to about 25% of the volume of mortars used as tile adhesives [7].

Mortars with CE additions acquire a thickened, creamy consistency and hence an improved and prolonged workability and stickiness to the substrate and the embedded tiles [1,3]. At the same time, the entrained air reduces the density of the mixture, which is important not only in terms of improved workability, but also during application of the mortar on walls or ceilings. Finally, thanks to the entrained air, the mortar can be easily compressed when the tile is embedded, which allows for easier leveling of the tile.

1.2. Influence of CE on the microstructure of the mortars

The structure of the entrained air voids has been analyzed in detail in [5,7] and its evolution in time due to different CE additions in [8,9]. Albeit air-entrainment is an usual consequence of CE addition [5,8] and the mechanisms of air entrainment in cementitious materials are generally well understood [5,6], it is not fully recognized whether and to which extent CE addition influences the pore structure of the cementitious matrix, i.e., the gel and the capillary pores. Capillary pores (about 10 nm–1 μm) are the remnants

of the originally water-filled spaces between cement particles in the fresh mixture, while gel pores (smaller than about 10 nm) are the smaller pores within the hydration products, mainly within the C–S–H gel [10,11].

Controlling the matrix porosity may be extremely important, since the matrix porosity is fundamental for water migration to the mortar interfaces (with substrate, tile and air), shrinkage and cracking in the hardening mortar [10,12,13]. It was found in [9] that CE addition reduces water permeability in model hardened cement pastes. This permeability reduction was attributed to the entrained air interrupting the otherwise continuous passages in which capillary flow of water takes place. Nevertheless, the effect of CE on the porosity of the cementitious matrix was not addressed. Moreover, the positive effect on limiting water transport concerned only one transport scenario (capillary flow in capillary pores and vapor diffusion in air voids) and did not account for the possible interconnectivity of a large part of the air voids, see also [14].

In addition to the entrained air pores, CE may impact the microstructure of the matrix by affecting the hydration process of cement in different ways. First, retardation of cement hydration due to addition of macromolecular CE has been widely observed, e.g. [15–21]. At the same time, some studies found a higher final degree of hydration for CE modified mortars due to better dispersion of cement during mixing [20]. Further, CE addition improves water retention in fresh mortars [22–25]. This may potentially improve further hydration if water is held in a hydrating mortar for longer time. Delaying effect of CE on carbonation kinetic was also reported, which may consequently also influence the pore structure as it is modified by carbonation process [21,26].

Finally, it was suggested that the CE presence modifies the pore structure of the cementitious matrix due to deposition of polymers in the pores [27].

In this study, we used mercury intrusion porosimetry (MIP) to investigate the pore structure in model tile adhesive mortars prepared with addition of only CE (without e.g. redispersible polymer powders). Three different CE were used: Methyl Cellulose (MC), Hydroxyethyl Methyl Cellulose (HEMC) and Hydroxypropyl Methyl Cellulose (HPMC), at two addition rates (by mass of dry mortar): 0.3% and 0.8% (see Tables 1 and 2).

1.3. Mercury Intrusion Porosimetry

The pore size distribution (PSD) was analyzed using MIP. In MIP, the pore size distribution is obtained indirectly by measuring the amount of mercury that is intruded into a porous material at given pressure levels. At this point, using the geometrical model of porosity by Washburn [28], the sizes of equivalent, cylindrical model pores can be calculated. The relevance of the results obtained by means of the conventional MIP technique in the case of cementitious systems has been criticized [28], mainly due to the presence of the so-called ink-bottle effect, which leads to a systematic misinterpretation of the pore sizes. Ink-bottle pores are larger voids which can be accessed by smaller neck-entrances only. In conventional MIP the volume of ink-bottle pores may be erroneously attributed to the sizes of their smaller entrances.

The problematic interpretation of conventional MIP in the presence of ink-bottle pores is crucial for tile adhesive mortars, due to their large volume fraction of entrained air, which is a good example of ink bottle porosity. In previous publications devoted to porosity in CE-modified tile adhesive pastes or mortars, the ink-bottle artifact led to erroneous interpretation of the MIP results [9,27,29], where large air voids that could only be accessed through capillary-size entrances were interpreted as actual capillary voids. On the other hand, the amount of air voids in those studies was grossly underestimated, as only the porosity accessed by mercury through large radii was assigned to the air voids. We suggest that a large part of the entrained air voids is not necessarily interconnected and connected to the surface. Therefore, the air voids in the inner part of a mortar specimen must be accessed by the mercury through smaller capillary entrances, [28,30].

One of the methods that have been developed to account for the ink-bottle effect and obtain meaningful size distributions of interconnected gel and capillary porosity is the multi-cycle MIP technique [30], also referred to as the pressurization–depressurization cycling MIP (PDC-MIP) [31]. The key assumption of this method is that, after the first intrusion–extrusion cycle, all ink-bottle voids remain filled with mercury. Thus, during the second intrusion, only the interconnected porosity of the matrix is refilled with mercury.

1.4. Application of mortars

In addition to different types of CE studied, the pore structure of mortars applied to different substrates was investigated, in order to separate the influence of CE itself from the effects of specific maturing conditions. Three types of scenarios were tested, Table 3: (1) application in a flat layer on a non-absorbing substrate, (2) same as (1), but applied on an absorbing substrate (cement–fiber boards), and (3) mortars applied on an absorbing concrete slab, combed with a notched trowel and with tiles embedded on top. For the model scenarios 1 and 2, the samples were sealed after

Table 1
CE formulations tested.

Designation	Type	Degree of substitution (DS) [38]	Viscosity[a] (mPa s)	Molar degree of substitution (MS)
MC	Methyl Cellulose	1.88	4640	–
HEMC	Hydroxyethyl Methyl Cellulose	1.86	3600	0.16
HPMC	Hydroxypropyl Methyl Cellulose	1.87	4100	0.17

[a] Measured as 2% aqueous solution with a Haake Rotovisko viscometer, $D = 2.5 \text{ s}^{-1}$.

Table 2
Materials tested.

Mixture	CE used	Water/solid ratio	Water/cement ratio	CE dosage (mass % of dry mortar)	CE concentration in water (mass %)
REF	–	0.20	0.67	0	0
MC 03 HEMC 03 HPMC 03	MC HEMC HPMC	0.20	0.67	0.3	1.5
MC 08 HEMC 08 HPMC 08	MC HEMC HPMC	0.24	0.81	0.8	3.3