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Influences of superplasticizer, polymer latexes and asphalt emulsions on the pore structure and impermeability of hardened cementitious materials

Yanrong Zhang, Xiangming Kong *

Department of Civil Engineering, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- The chemical admixtures affect the pore structure due to their plasticizing effects.
- Superplasticizer enhances the impermeability of mortar due to its plasticizing effect.
- Polymers raise the impermeability due to combined effects of filling and plasticizing.
- Filling effect is dominating the enhancement in impermeability at high P/C value.
- Mortars with latex L1 and anionic asphalt emulsion are superior in impermeability.

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ABSTRACT

Three types of polymers commonly used in concrete and mortar (polycarboxylate superplasticizer, polyacrylate latexes and asphalt emulsions) which differ in molecular/particle size from nanometer to micron were employed to investigate their effects on the pore structure of hardened cement pastes and the impermeability of hardened mortars. The pore structure and the impermeability of the hardened ones cured for 7 days and 28 days were measured by mercury intrusion porosimetry and alternating current impedance, respectively. Results show the incorporation of superplasticizer obviously reduces the average pore size and enhances the impermeability. The polyacrylate latexes also lead to the decline in pore size and consequently the enhanced impermeability at dosage higher than 3%. At the same dosage, latex with smaller polymer particle size is more effective in reducing the average pore size and enhancing the impermeability than that with larger particle size due to its better plasticizing effect. Similarly, asphalt emulsions also facilitate the enhancement in impermeability, and the anionic asphalt emulsion with better plasticizing effects brings about stronger impermeability than the cationic one. It is believed that for superplasticizer, the plasticizing effect is the main controlling factor for the finer pore structure and the enhanced impermeability. In the case of polymer latexes and asphalt emulsions, the plasticizing effect contributes actively at low dosage and the filling effect is dominant at high dosage in terms of declining pore size and augmenting impermeability.

1. Introduction

Concrete, being the most widely used construction material, has drawn increasing research interests and attentions on its durability [1–3]. Recently, many investigations have been conducted to improve the durability of concrete [1–7]. It has been well accepted that most issues regarding concrete durability are related to the permeability of concrete, such as freeze–thaw deterioration, chloride ingress, sulfate attack, and carbonation [8]. In general, increasing concrete impermeability is the key to increase the durability [9]. The impermeability of concrete is primarily determined by the pore structure of cement pastes, and is also affected by cracks and interfaces between the cement pastes and aggregates [10,11].

Various polymers have been incorporated in modern concrete in order to achieve desired properties. For example, adding superplasticizers into fresh cementitious materials can improve their rheological properties and thus in the premise of satisfying the construction requirements, lower water to cement ratio (W/C) could be achieved. As well known, the lower W/C is required to produce concrete with higher strength, lower permeability, and higher durability [12,13]. Khatib and Mangat [14] reported that

* Corresponding author. Tel.: +86 10 62783703; fax: +86 10 62785836.
E-mail address: kxm@tsinghua.edu.cn (X. Kong).

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superplasticizers were beneficial to the refinement of pore structure at a constant W/C. Sakai et al. [15] discussed the influence of various types of superplasticizers on the pore structure and found that the size of the cluster of aggregated cement particles became smaller when superplasticizer with a higher dispersing ability was added. Polymer latexes are often used as cement mortars and concrete modifiers to improve mortars and concrete properties such as adhesion, fracture toughness, flexural strengths, crack resistance and waterproof [16,17]. Ohama and Demura [18] revealed oxygen diffusion resistance of the polymer-modified mortars is larger than that of unmodified mortars, and is markedly increased with an increase in polymer to cement ratio. Moreover, Gao et al. [19] found that the pore volume and the pore size of latex-modified cement pastes tended to become smaller with an increase in latex to cement ratio because the capillary pores of the hardened cement pastes were filled in with the polymer particles or the polymer membranes formed by agglomeration of the polymer particles. Meanwhile, the polymer latex film could effectively compact the interfacial zones between fine aggregates and cement pastes [20–22], enhancing the impermeability of hardened mortars [23]. Cement asphalt mortar (CAM) is one kind of inorganic–organic composite which is composed of Portland cement, asphalt emulsions, water, fine aggregates, and other admixtures. With high elasticity and desired toughness, CAM serves as a vibration-absorbing layer in the slab track system of railroad structures. The properties of CAM have significant effects on slab track performances [24,25]. As a necessary component, asphalt emulsions greatly influence the properties of CAM, such as mechanical properties, temperature sensitivity, and microstructure. [26–28]. Especially, the covering of hydrophobic asphalt emulsions on cement grains could increase the impermeability of CAM to some extent [29].

These polymers, which are widely used in cementitious materials, have different particle sizes. Polycarboxylate (PC) superplasticizer usually has a hydraulic radius of 10–100 nm in aqueous solution. The particle size of polymer latexes ranges from 100 to 1000 nm, while the particle size of asphalt emulsions is usually in the range of 1–10 μm. Although much research on the cement mortar with superplasticizer, polymer latex and asphalt emulsion have been conducted, few studies dwell on their impacts on the pore structure and the impermeability from the viewpoints of microstructure in the fresh state of cement paste, especially their different impacts originating from the particle size. Specifically, the formation of the pores may be affected by addition of these polymers due to their impacts on the rheological properties of fresh pastes, cement hydration, and the shrinkage of hardened pastes. Furthermore, the type of polymers with varied particle sizes also plays an important role in changing the pore structure and the impermeability. It is supposed that these polymers may affect the pore structure and the impermeability from three perspectives: (1) changing the flocculation microstructure of cement grains, which is demonstrated by the variations of the fluidity of fresh pastes in macro scales; (2) altering cement hydration process; (3) filling the pores and the cracks in the transition zones and forming films in many cases.

In this study, PC superplasticizer, polyacrylate latexes and asphalt emulsions were incorporated into cement pastes and mortars to investigate their impacts on the pore structure and the impermeability. The pore structure of the cement pastes and the impermeability of the mortars cured for 7 and 28 days were tested by mercury intrusion porosimetry (MIP) and alternating current (AC) impedance, respectively. By analyzing the changes in the pore structures and the impermeability with varied polymer dosages and types, the working mechanisms of superplasticizers, polyacrylate latexes and asphalt emulsions were discussed.

2. Experimental

2.1. Materials

Portland cement P·I 42.5 which complies with the Chinese standard GB8076-2008 from Lafarge Shui On Cement Co., Ltd. was used, whose compositions are listed in Table 1. The fineness of the cement is 0.5 and the density is 3.10 g cm^{-3}. A self-synthesized PC superplasticizer was employed, whose properties are shown in Table 2. Two different styrene–acrylate copolymer latexes (latex L1 and latex L2 with different particle sizes and T_g) produced by BASF (China) Co., Ltd. were used, the properties of which are listed in Table 3. Two types of anionic and cationic asphalt emulsions (whose properties can be seen in Table 4) were provided by China Petrochemical Corporation. Both standard sand (complying with GB178) and 40–70 mesh quartz sand were used for the preparation of mortar specimens. RHODOLINE DF 642, antifoaming agent, was provided by Rhodia (China) Co., Ltd.

2.2. Specimens preparation and measurements

Cement pastes and mortars were prepared according to the formulations presented in Table 5. P/C is defined as the mass solid/solid ratio of polymer to cement. W/C is the water to cement ratio. In the formulations of cement mortars, the mass ratio of sand to the sum of cement and polymer is expressed as S/(C + P). The antifoaming agent to polymer ratio in all specimens was set at 0.0005. All specimens were prepared in a mixer equipped with paddles rotating helicoidally at successive speeds. The mixing procedure of cement pastes and mortars followed the Chinese standards GB/T8077 and GB/T17671-1999, respectively. Three different curing conditions were used: the standard curing condition (moist curing at 20 °C and 95% relative humidity (R.H.)), the dry curing condition (1-day moist curing and 27-day curing at 20 °C and 65% R.H.) and the mix curing condition (21-day moist curing and 7-day dry curing).

2.2.1. MIP measurement

The pore structure of the hardened cement pastes (HCPs) was determined by MIP. After being cured for 7 days or 28 days, the HCPs were cut into small pieces and placed into an alcohol bath. After 3-day storage in an oven with a controlled temperature of 60 ± 2 °C, they were subjected to MIP tests to determine the pore structure characteristics by using an Hg-porosimetry (Autopore, IV 9510, USA). The difference in mercury volume was determined by re-intruding mercury into pastes after the first intrusion-depressurization cycle was completed. A part of the intruded mercury was entrapped in the pores with certain geometric shapes, which were called inkbottle pores [30]. As well known, the addition of superplasticizers brings significant effects on the rheological properties of fresh cement pastes (FCPs) by modifying their microstructures. Information on the pore structure of HCPs especially at early age could provide understanding on the microstructures of FCPs. It has been reported that the entrapped mercury pores in FCPs is related to the flocculation structure of cement grains in FCPs [15]. Therefore, two cycles of intrusion-extrusion were performed and the inkbottle pores volume was calculated as follows [15]: $V_{ib} = V_1 – V_2$, where V_1 is the volume of mercury intruded during the first cycle, and V_2 is the volume of mercury intruded during the second cycle.

2.2.2. AC impedance measurement

AC impedance spectroscopy technique has been widely used to investigate the microstructure and the permeability of hardened cementitious materials based on the relationships between the parameters of AC impedance and the structure of

Table 1
Composition of Portland cement (wt%).

SiO_2	Fe_2O_3	Al_2O_3	SO_3	MgO	CaO	Na_2Oeq
21.56	2.78	4.44	3.14	2.32	62.83	0.6
f-CaO	Cl^-	IL	C_3S	C_2S	C_4AF	C_3A
0.79	0.007	2.04	46.00	27.14	8.45	7.05

Table 2
Properties of PC superplasticizer.

Solid content (%)	Hydrodynamic radius (nm)	Component	Mn	Mw/Mn	Density (g/cm^3)
40	8	Poly (AA-co-MEPEGMA-co AMPS)	3.662×10^4	2.482	1.04

Note: Hydrodynamic radius of polymer chain in aqueous was measured by dynamic laser scattering. Molecular weight of polymer was measured by gel permeation chromatograph.