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Effects of organo-modified montmorillonite on strengths and permeability of cement mortars

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Abstract

Organo-modified montmorillonites (OMMT) which have been widely used in polymer/clay nano-composites are employed here as fillers and reinforcements in cement mortars. The ratio of quartz sand and cement is 2.75 while the water/cement ratios of 0.40, 0.485 and 0.55 are considered for the cement mortars we studied. Experimental results indicate that the coefficients of permeability of cement mortars could be 100 times lower if a lower dosage of OMMT micro-particles is added. At the same time, the compressive and flexural strengths of cement mortars can be even increased up to 40% and 10%, respectively. It is also found that the optimal dosage of OMMT micro-particles to give higher compressive and flexural strengths and a lower coefficient of permeability for cement mortars is less than 1%. Meanwhile, the microstructure of cement mortars is characterized by using SEM, EDS and MIP to evaluate the effects of OMMT micro-particles on the improvements of strengths and permeability of cement mortars.

Keywords: Organo-modified montmorillonite; Strength; Permeability; Cement mortar

1. Introduction

The overall porosity and pore size distribution in cement paste, which are mainly influenced by the water/cement ratio of a mix design, play an important role in determining the mechanical properties of concrete. In cement paste, the porosity with a wide range of pore sizes from 10 μm to less than 0.5 nm in diameter can be simply classified into two groups [1]: capillary pores and gel pores. Gel pores within the volume of hydration product C–S–H are normally treated as intrinsic micro-defects of cement paste because they are typically less than 10 nm. On the contrary, capillary pores, which are the remnants of water-filled space between hydrated cement grains, are relatively larger and can be observed from scanning electron micrographs (SEM). Both capillary pores and gel pores in cement paste carry no loads, resulting in a reduction of compressive and flexural strengths of concrete. In addition, capillary pores are interconnected to form a channel through which pore solution and aggressive chemicals are more likely and easily to diffuse; gel pores, however, are too small for pore solution and aggressive chemicals to flow through. As a result, the permeability of concrete is primarily affected by the capillary pore size distribution in cement paste. Therefore, the effects of capillary pores on the strengths and permeability of concrete are more significant as compared to gel pores.

When both strength and durability are sought for modern concrete, some additives such as mineral components, chemical admixtures and reinforcements are needed to blend with a mixture of cement, water and aggregates [2]. For example, fly ash, slag and limestone [3], ground clay brick [4], metakaolin and calcined clays [5] were separately added to improve the hydration, microstructure and resulting mechanical properties of concrete. It is expected that the strengths and durability of a concrete could be enhanced if the overall porosity and capillary pore sizes in cement paste are reduced or the diffusion of pore solution and aggressive chemicals is hindered by the introduction of some additives with a similar range of capillary pore sizes. Therefore, the introduction of micro-particles in cement and concrete might lead to some ways of enhancing the strengths and durability of modern concrete. However, the application of nanotechnology in cement and concrete research has been paid less attention. In existing literature, Li et al. [6] reported that the compressive and flexural strengths of cement mortars containing

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Table 1
Physical and chemical properties of OMMT micro-particles

Physical properties		Chemical properties	
Specific gravity	1.66	Chemical composition (wt.%)	
Moisture content	<2%	Montmorillonite/quaternary ammonium salt	60:40
Average size	5 μm	Cation exchange capacity (meq/100 g)	125
Basal spacing, *d*00	30 Å		

SiO_2 and Fe_2O_3 nano-particles were both higher than those of plain cement mortar. Their experimental results suggested that some nano-particles could be used as reinforcements in cement and concrete. But, the microstructure of cement mortar reinforced with nano-particles was not observed and characterized in their study. Layered double hydroxide-like nanocomposites for use in concrete were synthesized and characterized by Raki et al. [7]; the effects of nano-composites on the mechanical properties of concrete were not investigated. Collepardi et al. [8] and Campillo et al. [9] verified that the compressive strengths of self compacting concretes and cement pastes can be significantly increased when colloidal silica nanoparticles are introduced as reinforcements.

Smectite clays composed of SiO_2, CaO and Al_2O_3 are the primary compounds for the sludge of dams and reservoirs in Taiwan. For the purposes of economy and ecology, the applicability of smectite clays as reinforcements in cement and concrete is of importance and should be exploited in detail. Smectite clays such as montmorillonite (MMT) are frequently used as fillers or reinforcements in polymer/clay nanocomposites (PCN) [10]. The typical chemical structure of MMT consists of an edge-shared octahedral sheet with aluminum or magnesium hydroxide and two silicate tetrahedral sheets with sodium or calcium cations, which can be chemically replaced by a cationic-exchange reaction. In practice, the interlayer sodium or calcium cations of MMT are exchanged for organic cations before synthesizing polymer/clay nanocomposites. As a result of that, the originally hydrophilic layered silicate sheets become organophilic. Furthermore, the organo-modified montmorillonite (OMMT) whose interlayer regions have been swollen with organic molecules due to the intercalation chemistry of silicate sheets can be dispersed compatibly with polymer matrix to form exfoliated PCN via a bulk polymerization technique [10–12]. For instance, each sheet of OMMT with a thickness of 1 nm in the well-known nylon 6-clay hybrids (NCH) [12] is delaminated and dispersed homogeneously in nylon 6 matrix. Consequently, the mechanical and thermal properties of NCH were found to be dramatically improved as compared to nylon 6 matrix.

The hydrophilic MMT micro-particles cannot be directly used as reinforcements in cement and concrete because water absorbed in the interlayer regions between silicate sheets will cause detrimental expansion to a certain extent. At the same time, the interlayer alkali cations of MMT micro-particles are harmful to the durability of cement mortar and concrete and should be replaced by some organic cations before they are mixed with water and cement. The OMMT micro-particles modified by a cationic-exchange reaction become hydrophobic and thus can be utilized to improve the microstructure and mechanical properties of cement mortar and concrete. Presumably, the hydrophobic OMMT micro-particles can prevent water from penetrating the interlayer regions between silicate sheets as observed in MMT micro-particles, leading to a lower water/cement ratio in a mix design. On the other hand, the OMMT micro-particles around capillary pores can obstruct the diffusion of pore solution and aggressive chemicals and thus reduce the permeability of cement mortar and concrete. In this paper, we aim at investigating the effects of OMMT micro-particles on the compressive strength, flexural strength and

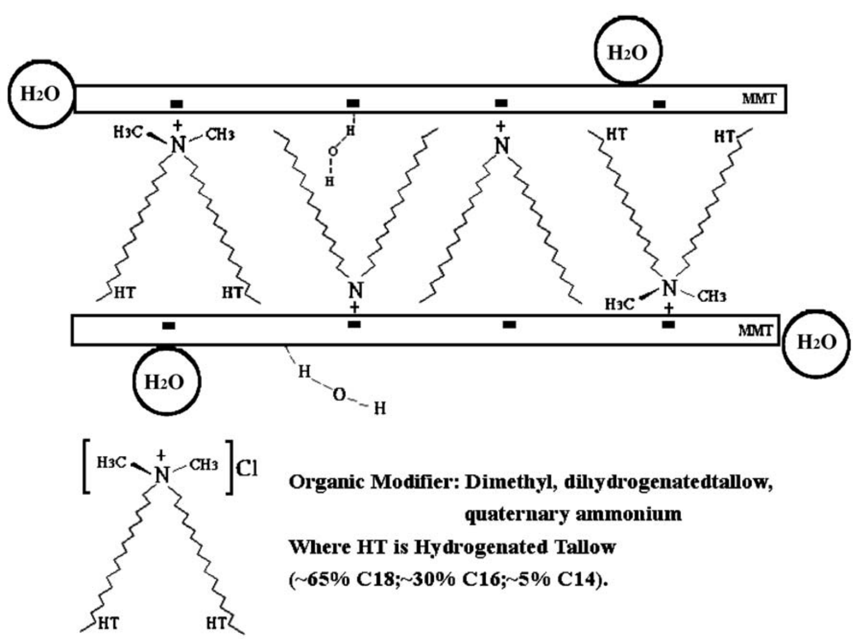


Fig. 1. The schematically illustrated chemical structure of OMMT micro-particles modified by the organic modifier of dimethyl dihydrogenatedtallow quaternary ammonium chloride.

coefficient of permeability of cement mortars. By conducting a series of compression, bending and permeability tests, the optimal dosage of OMMT micro-particles will be determined. Meanwhile, the microstructures of cement mortars reinforced with different dosage of OMMT micro-particles will be investigated and characterized by using SEM, mercury intrusion porosimetry (MIP) and energy dispersion spectrometer (EDS) to provide some physical insight.

2. Materials and methods

The OMMT micro-particles, purchased from MesoPhase Technologies, Inc., Taiwan, are modified from purified sodium MMT micro-particles by using the organic modifier of dimethyl dihydrogenatedtallow quaternary ammonium chloride, which is a commercially available swelling agent in synthesizing polymer/clay nano-composites. The physical and chemical properties of the OMMT micro-particles measured by means of XRD and chemical analysis provided by MesoPhase Technologies, Inc., Taiwan, are listed in Table 1. The chemical structure of OMMT micro-particles as schematically illustrated in Fig. 1 indicates that some absorbed water might be on the outer surfaces of silicate sheets and only little water could exist in the interlayer regions between silicate sheets by way of hydrogen bonding. The SEM micrographs of a single particle of MMT and OMMT are shown in Figs. 2 and 3, respectively. It is seen that the particle size of ball-milled OMMT micro-particles with an irregular and layered microstructure is slightly smaller than that of purified sodium MMT micro-particles; the average particle size of OMMT micro-particles is around 5 μm. The OMMT micro-particles, whose interlayer regions between silicate sheets were swollen by the organic modifier of dimethyl dihydrogenatedtallow quaternary ammonium chloride, possess a fluffy appearance while the purified sodium MMT micro-particles without any organic modifier have a closely knit surface. In order to verify that the hydrophilic MMT micro-particles become hydrophobic after being modified by the organic modifier, thermogravimetric analysis (TGA) on the MMT and OMMT micro-particles will be first conducted and then compared to each other.

In this paper, the constituent materials of cement mortars include water, quartz sands, type I portland cement and OMMT micro-particles; the physical and geometrical properties of quartz sands are listed in Table 2. It is noted that the size distribution of quartz sands is quite uniform and their mean size, roughly equal to 600 μm, is much larger as compared to that of OMMT micro-particles. Since OMMT micro-particles with a relatively higher surface area per unit volume are difficult to mix simultaneously with water, cement and quartz sands, the microstructure and mechanical properties of cement mortars reinforced with OMMT micro-particles are significantly influenced by the mixing procedure of their constituent materials. Hence, OMMT micro-particles were at first mixed solely with water. At the same time, the pH value of mixing water was adjusted to about 3–4 by the addition of 1 M phosphoric acid aqueous solution. The OMMT micro-particles in a cluster should be stirred vigorously at room temperature for at least 12 h to form a well-dispersed suspension solution before cement grains were added. Finally, quartz sands were added to the cement slurry with well-dispersed OMMT micro-particles. For the cement mortars we produced, the ratio of quartz sands and cement was fixed and equal to 2.75 while the water/cement ratios of 0.4, 0.485 and 0.55 were of concern. The dosages of OMMT micro-particles expressed as a weight fraction of replacement for cement in a mix design were 0.0625, 0.125, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0, 5.0 and 10%. For comparison, cement mortars without any OMMT micro-particles were also produced for the three water/cement ratios of 0.4, 0.485 and 0.55.

The wet cement mortars were cast into steel molds after complete mixing. One day later, the cement mortar specimens were removed from steel molds and cured in water at room temperature for additional 6 days or 27 days. At first, the

Table 2
Physical and geometrical properties of quartz sands

Physical properties		Grading of quartz sands	
		Sieve size	Amount retained (wt.%)
Specific gravity	2.65	#4	0.00
Moisture content (%)	0.08	#8	0.02
Average size (μm)	600	#16	2.57
Fineness modulus	2.98	#30	93.13
		#50	4.14
		#100	0.08
		Pan	0.06

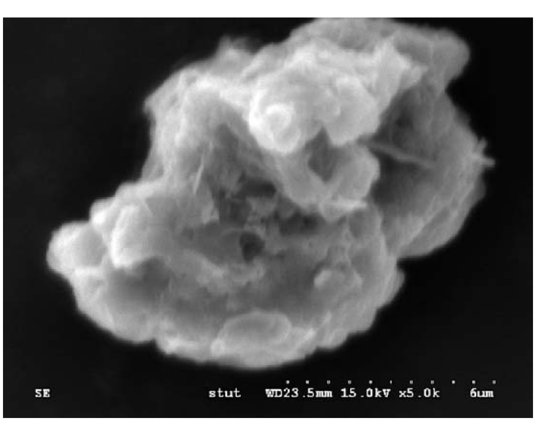


Fig. 2. SEM micrograph of a single MMT particle.

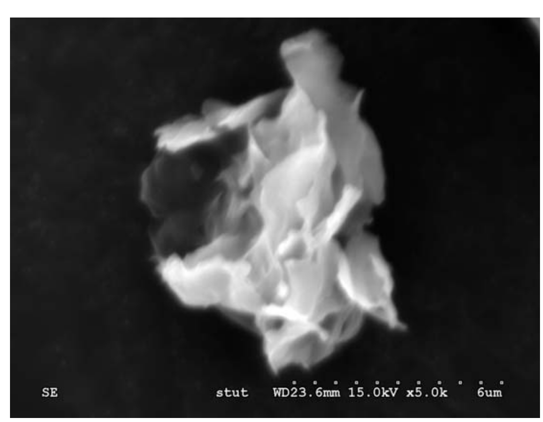


Fig. 3. SEM micrograph of a single OMMT particle.

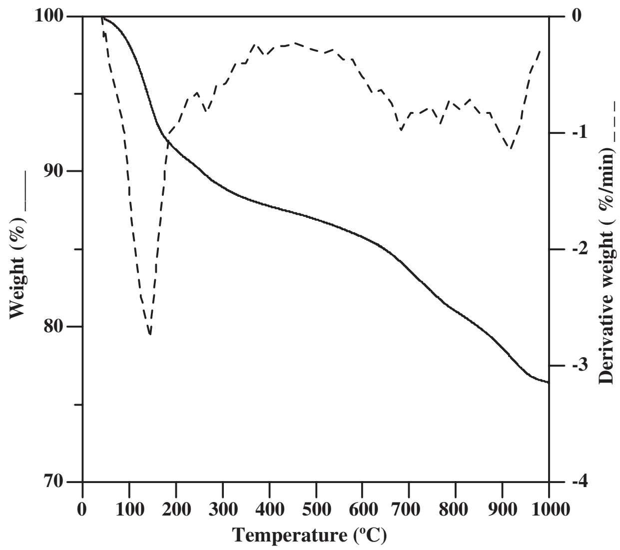


Fig. 4. Experimental result of thermogravimetric analysis on purified sodium MMT micro-particles.

microstructure of cement mortars reinforced with OMMT micro-particles was observed by using SEM while the locations of OMMT micro-particles around capillary pores were identified by using EDS. Meanwhile, the cement mortar specimens with a volume of 10 mm × 10 mm × 15 mm were first dried in an oven heated to 110 °C and then placed in a chamber of mercury intrusion porosimetry; the dosages of OMMT micro-particles studied here were 0%, 0.5% and 2%. The variation of total weight for each specimen was recorded as the pressure in the chamber was increased from zero up to roughly 400 MPa. As a result, the pore size distribution of the specimen we measured was obtained.

Cement mortar specimens cured in water were dried and then trimmed before mechanical testing. The specimen sizes of cement mortars are 50 mm × 50 mm × 50 mm for compression tests and 40 mm × 40 mm × 160 mm for three-point bending tests. During mechanical testing, the 7-day and 28-day cubic specimens were loaded under a rate of 300 kPa/s while the 7-day and 28-day beam specimens were bent under a rate of 2.64 kN/min. In addition, the 28-day cylindrical specimens with a diameter of 50 mm and a height of 100 mm were tested for measuring the coefficients of permeability of cement mortars reinforced with different dosages of OMMT micro-particles. The cylindrical specimens were placed in a triaxial cell under a confining pressure of 250 kPa and a differential pressure of

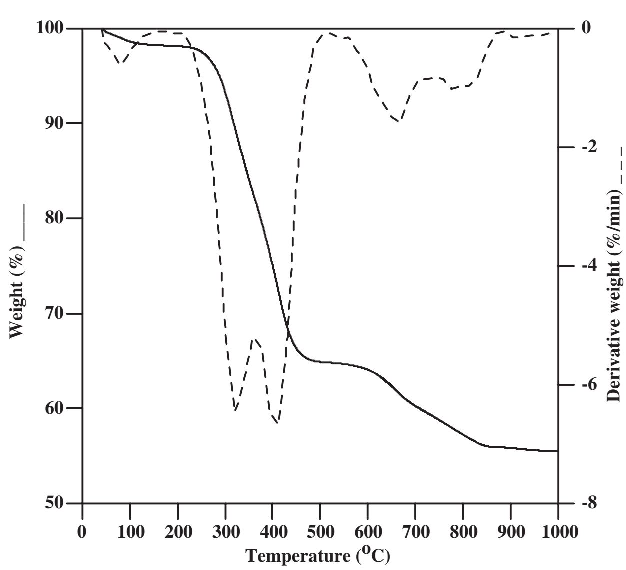


Fig. 5. Experimental result of thermogravimetric analysis on OMMT micro-particles.

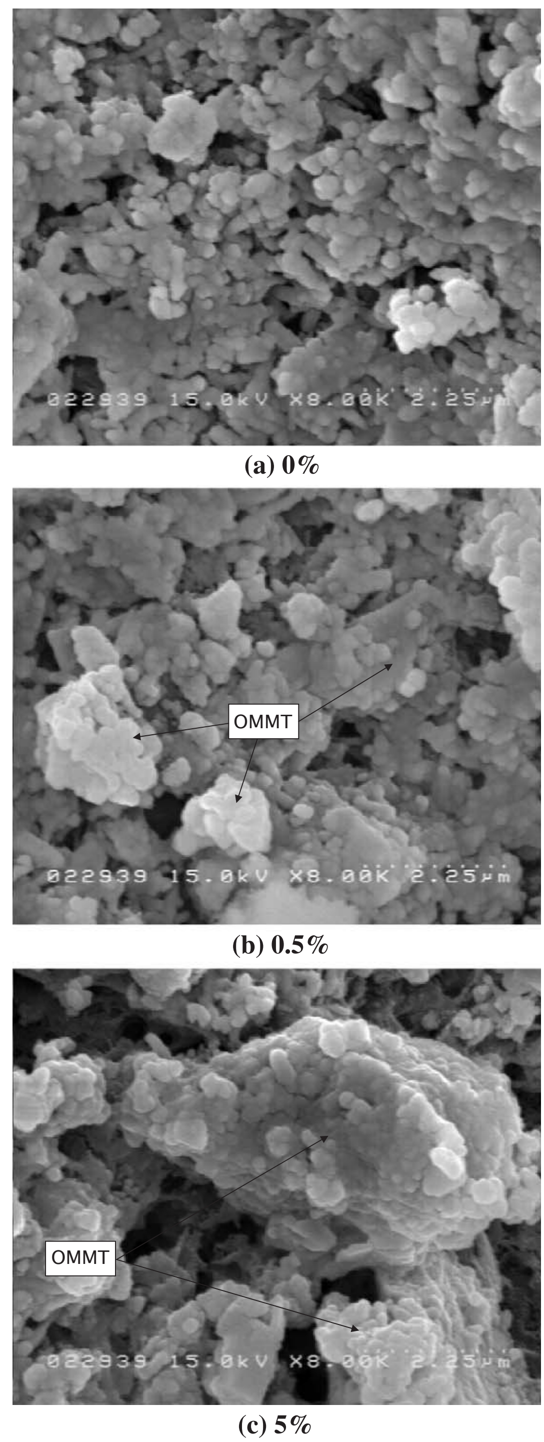


Fig. 6. SEM micrographs of a cement mortar reinforced with (a) 0%, (b) 0.5% and (c) 5% OMMT micro-particles when the water/cement ratio is 0.485.

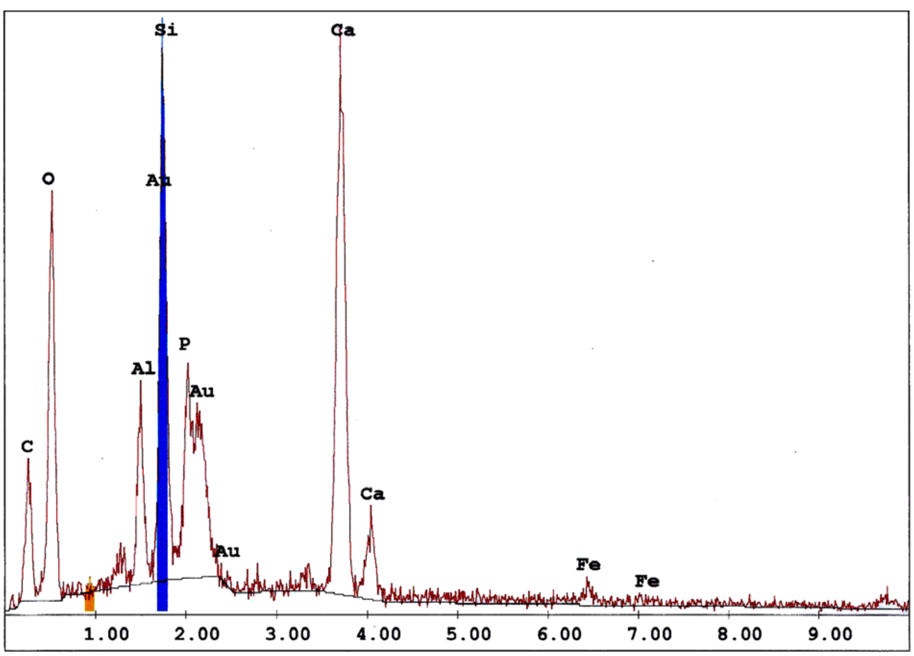
100 kPa between top and bottom drain pressure systems. The coefficient of permeability of each cylindrical specimen was obtained from the measured amount of water passed through at a given time.

3. Results and discussion

3.1. Microstructural characterization

Experimental results of thermogravimetric analysis (TGA) on the MMT and OMMT micro-particles are shown in Figs. 4 and 5, respectively. From Figs. 4 and 5, it is seen that the amount of absorbed water, evaporated at around 150 °C, in the interlayer regions between silicate sheets for MMT micro-particles is much larger than that for OMMT micro-particles. Meanwhile, the organic modifier of dimethyl dihydrogenated-tallow quaternary ammonium chloride in the interlayer regions between silicate sheets of OMMT micro-particles is decomposed at the temperatures from 300 °C to 400 °C. Hence, it is verified that the OMMT micro-particles we used here have been modified and become hydrophobic before they are mixed with water and cement.

The effect of OMMT micro-particles on the microstructure of cement mortars can be observed from their SEM micrographs; for example, the SEM micrographs of cement mortars reinforced with 0%, 0.5% and 5% OMMT micro-particles when w/c = 0.485 are shown in Fig. 6(a), (b) and (c), respectively. The locations of OMMT micro-particles around capillary pores in each specimen were identified by using EDS and then marked in the SEM micrographs. The OMMT micro-particles around capillary pores in Fig. 6(b) and (c) are identified by EDS analyses from their peak values of carbon, oxygen, aluminum and silicon; a typical EDS result of the OMMT micro-particles around capillary pores is shown in Fig. 7. By comparing the microstructure of Fig. 6(b) to that of plain cement mortars in Fig. 6(a), it is found that the OMMT micro-particles could act as diffusion barriers around capillary pores for cement mortars reinforced with a lower dosage of OMMT micro-particle. But, clusters of OMMT micro-particles around capillary pores as observed in Fig. 6(c) will form for cement mortars with a higher dosage of OMMT micro-particles. Based on our experimental results, it can be concluded that clusters of OMMT micro-particles in cement mortars are more likely to occur when the dosage of OMMT micro-particles is larger than 1%.



EDAX PhiRhoZ Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	25.77	40.64	0.0497	1.1156	0.1727	1.0004
O K	35.61	42.15	0.0494	1.0593	0.1310	1.0002
AlK	2.96	2.07	0.0155	0.9503	0.5477	1.0056
SiK	8.42	5.68	0.0532	0.9742	0.6457	1.0037
P K	3.93	2.40	0.0245	0.9389	0.6605	1.0029
AuM	10.23	0.98	0.0806	0.6842	1.1505	1.0005
CaK	12.16	5.75	0.0993	0.9371	0.8705	1.0005
FeK	0.92	0.31	0.0076	0.8463	0.9702	1.0101
Total	100.00	100.00				

Fig. 7. A typical EDS result of the OMMT micro-particles around capillary pores.

The mercury intrusion porosimetry curves for 28-day plain cement mortars and cement mortars reinforced with 0.5% and 2% OMMT micro-particles are shown in Fig. 8. In MIP measurements, the pressure required to force mercury into a pore system is inversely proportional to its pore size; typically, a simple spherical geometry for the pore system should be assumed. As a result, the effective size of access, or equivalent diameter, and accessible total pore volume for the pore system under any pressure from 0 to 400 MPa can be computed and then plotted in a figure. From the three curves in Fig. 8, it can be seen that the pore size distribution of cement mortars is significantly influenced by the introduction of OMMT micro-particles. When the dosage of OMMT micro-particles is increased from 0 to 0.5%, the total volume of accessed pores is reduced. On the contrary, the total volume of accessed pores is increased as the dosage of OMMT micro-particles is increased from 0.5% to 2%. It is also found that the volume of pores larger than 0.5 μm is slightly increased, but the size distribution of pores smaller than 0.1 μm is less affected as the dosage of OMMT micro-particles is increased from 0 to 2%. The reason for that might be due to the difficulty in mixing cement slurry with clusters of OMMT micro-particles, resulting in an increase for the volume of larger pores. Meanwhile, the accessible pore volume of intermediate pores, larger than 0.1 μm but less than 0.5 μm, is significantly reduced for cement mortars reinforced with 0.5% and 2% OMMT micro-particles as observed in Fig. 8. It is attributed to the obstruction of OMMT micro-particles around capillary pores with a pore size from 0.1 to 0.5 μm when mercury is forced to flow into the cement mortar specimens in MIP tests.

3.2. Compressive and flexural strengths

The measured 7-day and 28-day compressive strengths of cement mortars reinforced with various dosages of OMMT micro-particles for the water/cement ratios of 0.4, 0.485 and 0.55 are shown in Figs. 9–11, respectively; in each case, three cement mortar specimens were measured and then averaged. Experimental results of the 7-day and 28-day compressive strengths for cement mortars with a water/cement ratio of 0.485 are listed in Table 3. From the figures, it is seen that the 7-day and 28-day compressive strengths of cement mortars increase initially and then decrease dramatically after reaching a peak value as the dosage of OMMT micro-particles is increased up to 10%. As compared to the 28-day compressive strengths of plain cement mortars, the increase of 28-day compressive

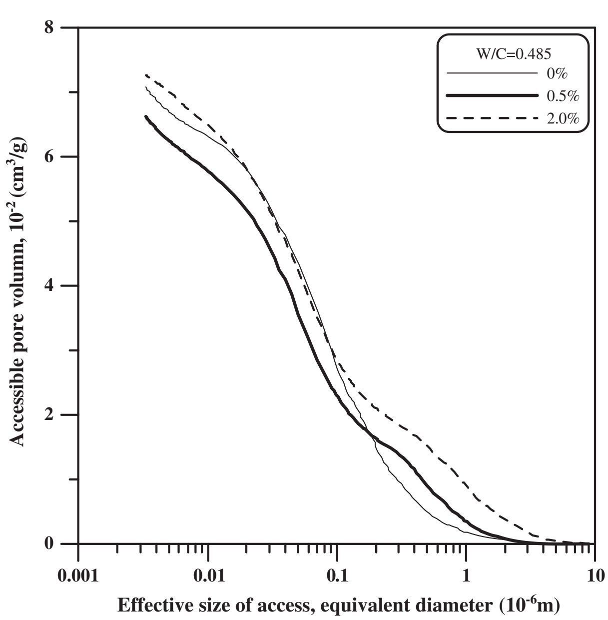


Fig. 8. Mercury intrusion porosimetry curves of cement mortars reinforced with 0%, 0.5% and 2% OMMT micro-particles.

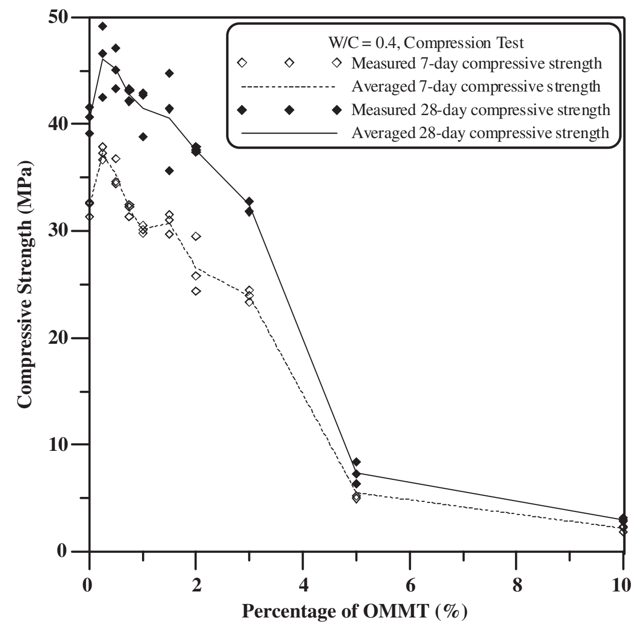


Fig. 9. Variation of compressive strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.4.

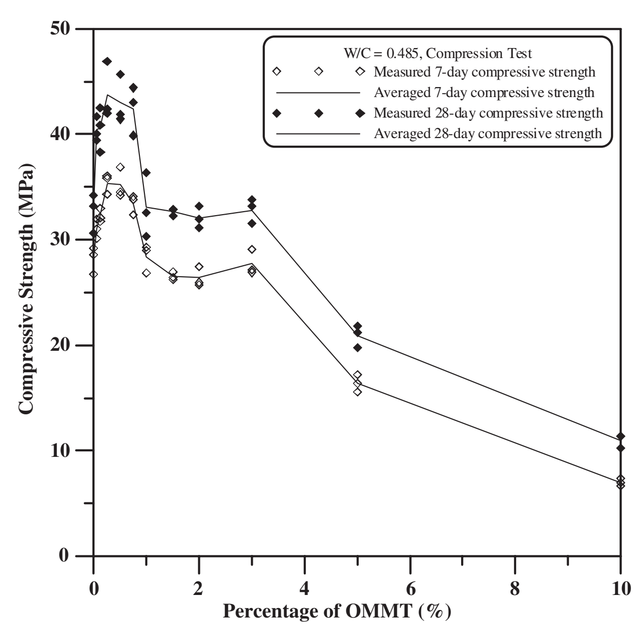


Fig. 10. Variation of compressive strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.485.

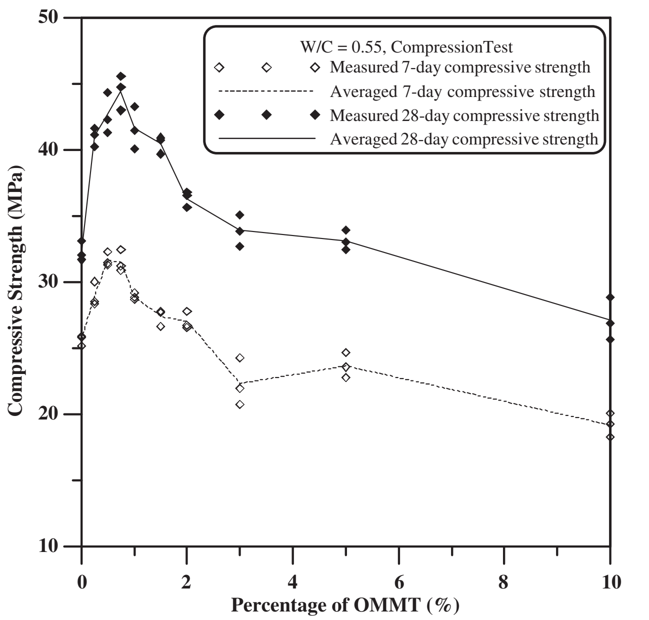


Fig. 11. Variation of compressive strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.55.

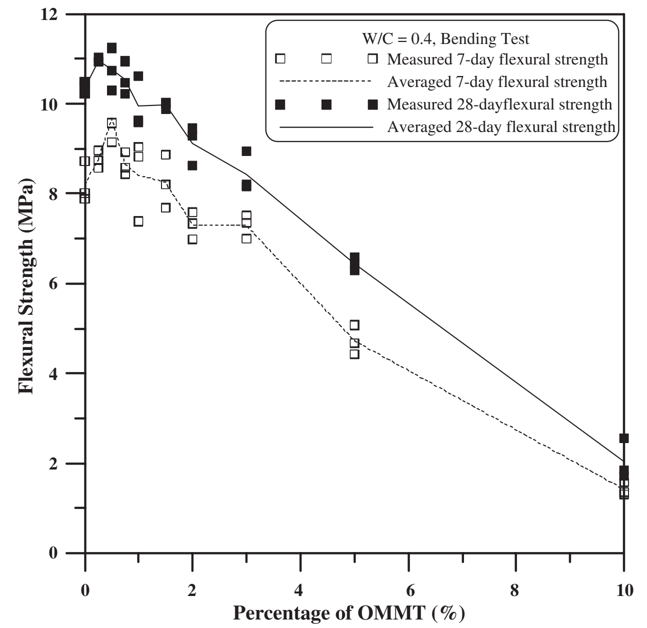


Fig. 12. Variation of flexural strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.4.

strengths of cement mortars reinforced with OMMT micro-particles can be up to 15% when w/c = 0.4, 34% when w/c = 0.485 and 38% when w/c = 0.55.

Similarly, the measured 7-day and 28-day flexural strengths of cement mortars reinforced with various dosages of OMMT micro-particles when the water/cement ratios of 0.4, 0.485 and 0.55 are shown in Figs. 12–14, respectively; experimental results of the 7-day and 28-day flexural strengths for cement mortars with a water/cement ratio of 0.485 are also listed in Table 3. Again, the 7-day and 28-day flexural strengths of cement mortars increase at the beginning and then drop after reaching a maximum as the dosage of OMMT micro-particles is increased. From Figs. 12–14, it is found that the flexural strengths for cement mortars reinforced with 0.125–1% OMMT micro-particles could be 10% greater than those of plain cement mortars. Although the optimal dosages of OMMT micro-particles for cement mortars are still less than 1%, their dependences on the water/cement ratio for flexural strengths, however, are slightly different from those for compressive strengths.

From Figs. 9–14, it is noted that the increases of compressive strengths for cement mortars with lower dosages of OMMT micro-particles are much larger than those of flexural strengths. The reason for that is because the compressive strengths are primarily controlled by the total porosity in cement mortars while the flexural strengths are affected by the critical pore size as well as the total porosity. Based on our MIP experimental results of Fig. 8, it is known that the total porosity is reduced but the critical pore size is increased when a lower dosage of OMMT micro-particles is added in cement mortars. As a result of those, the increase of

Table 3
Compressive strength, flexural strength and coefficient of permeability of cement mortars reinforced with various dosages of OMMT micro-particles when w/c = 0.485

Dosage of OMMT nano-particles (%)	Compressive strength ± SE (MPa)		Flexural strength ± SE (MPa)		Coefficient of permeability ($\times 10^{-8}$ cm/s)
	7-day	28-day	7-day	28-day	
0	28.16 ± 0.8	32.66 ± 1.1	9.86 ± 0.30	11.62 ± 0.14	6.75
0.0625	31.02 ± 0.5	40.40 ± 0.7	9.43 ± 0.20	11.99 ± 0.14	1.51
0.125	32.26 ± 0.4	40.56 ± 1.2	10.21 ± 0.17	12.77 ± 0.47	1.82
0.25	35.38 ± 0.5	43.75 ± 1.5	10.46 ± 0.15	12.48 ± 0.10	0.57
0.5	35.23 ± 0.8	43.00 ± 1.3	10.80 ± 0.25	12.74 ± 0.26	0.47
0.75	33.42 ± 0.5	42.44 ± 1.3	9.74 ± 0.08	12.50 ± 0.09	0.05
1	28.38 ± 0.8	33.08 ± 1.6	9.66 ± 0.29	12.84 ± 0.14	2.59
1.5	26.55 ± 0.2	32.69 ± 0.2	8.30 ± 0.17	10.31 ± 0.23	5.92
2	26.37 ± 0.5	32.08 ± 0.6	8.20 ± 0.56	10.59 ± 0.31	5.66
3	27.70 ± 0.7	32.85 ± 0.7	8.65 ± 0.23	10.89 ± 0.51	13.45
5	16.38 ± 0.5	20.94 ± 0.6	5.69 ± 0.06	6.64 ± 0.16	112.07
10	7.00 ± 0.2	10.97 ± 0.4	4.22 ± 0.08	6.53 ± 0.27	292.74

SE = standard error of the mean.

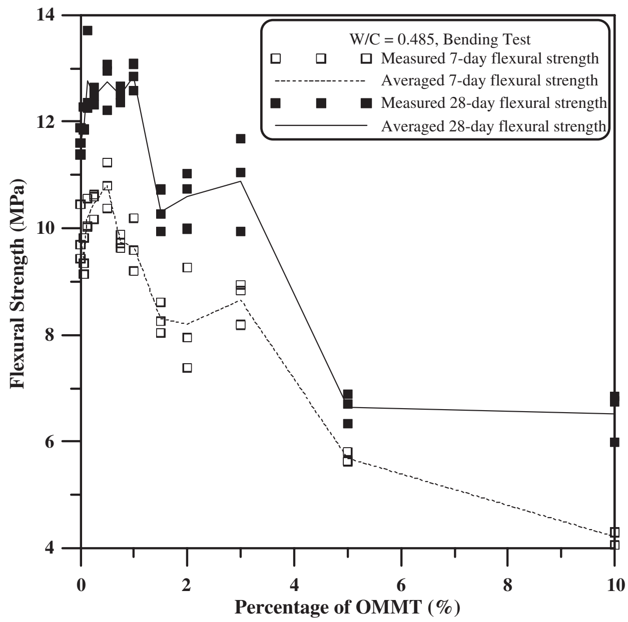


Fig. 13. Variation of flexural strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.485.

compressive strengths of cement mortars reinforced with a lower dosage of OMMT micro-particles could be up to 30–40%, but the increase of flexural strengths is only in the range of 5–10%.

3.3. Coefficient of permeability

Experimental results for the coefficients of permeability of cement mortars reinforced with various dosages of OMMT micro-particles when w/c = 0.485 are shown in Fig. 15 and also

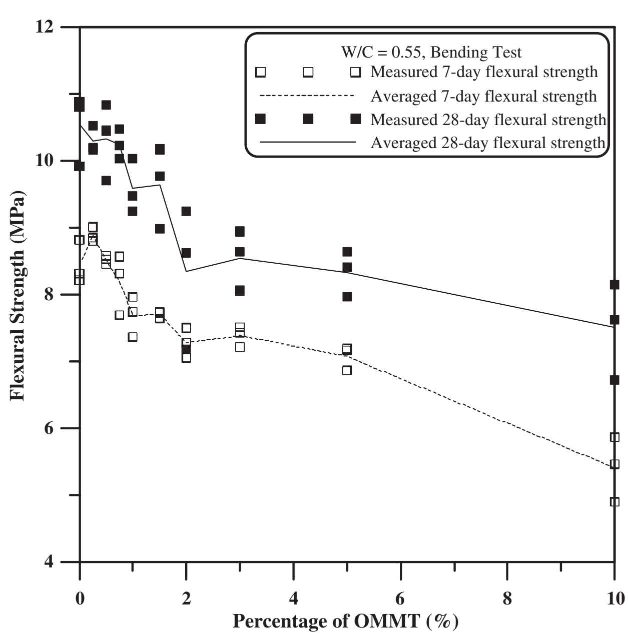


Fig. 14. Variation of flexural strengths of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.55.

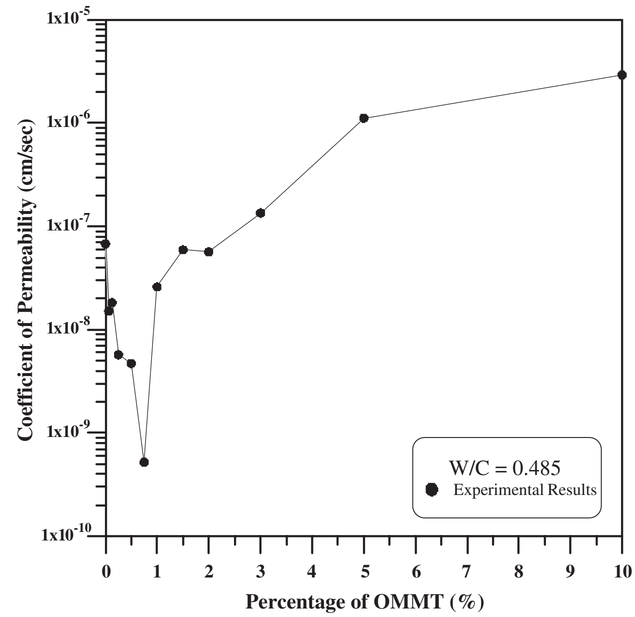


Fig. 15. Variation of coefficients of permeability of cement mortars reinforced with different dosages of OMMT micro-particles when the water/cement ratio is 0.485.

listed in Table 3. From Fig. 15, it is seen that the coefficients of permeability of cement mortars decrease at first and then increase rapidly after reaching a minimum value as the dosage of OMMT micro-particles is increased. In other words, the coefficients of permeability of cement mortars reinforced with a dosage of OMMT micro-particles less than 1% could be dramatically reduced; especially for cement mortars reinforced with lower dosages of 0.25, 0.5 and 0.75% OMMT micro-particles, their coefficients of permeability become 10–100 times lower. However, the coefficients of permeability of cement mortars reinforced with a dosage of OMMT micro-particles larger than 2% are relatively higher as compared to plain cement mortars. Again, the reason for that is due to the occurrence of clusters of OMMT micro-particles as the dosage of OMMT micro-particles is larger than 2%; a larger total porosity and critical pore size as observed in Fig. 8 can be expected. Since the effects of OMMT micro-particles on enhancing the compressive and flexural strengths of cement mortars are similar to those on reducing their coefficients of permeability, the coefficients of permeability are thus higher than those of plain cement mortars.

3.4. Optimal dosage of OMMT micro-particles

The improvements of strengths and permeability for cement mortars reinforced with low dosages of OMMT micro-particles are attributed to the decrease of capillary porosity within them. The capillary pore sizes ranging from 0.01 μm to 0.2 μm could be partially obstructed by the well-dispersed OMMT micro-particles with an average size of 5 μm, leading to the enhancements of strengths and durability. On the contrary, clusters of OMMT micro-particles surrounded by cement grains are more likely to form during the hydration process for cement mortars reinforced with higher dosages of OMMT micro-particles. Consequently, the strengths and durability become worse as the dosage of OMMT micro-particles is increased.

From Figs. 9–14, it is also seen that the optimal dosages of OMMT micro-particles for cement mortars with various water/cement ratios of 0.4, 0.485 and 0.55 are different. The optimal dosages of OMMT micro-particles for compressive strengths of cement mortars are less than 0.25% when w/c=0.4, 0.25–0.5% when w/c=0.485 and 0.5–0.75% when w/c=0.55; the optimal dosages of OMMT micro-particles for flexural strengths of cement mortars are 0.25–0.5% when w/c=0.4, roughly 0.5% when w/c=0.485 and 0.25–0.75% when w/c=0.55. Thus, it can be said that the optimal dosage of OMMT micro-particles approximately increases with the water/cement ratio in a mix design. The reason for that is because cement mortars with a higher water/cement ratio presumably have larger volume fraction and critical size of capillary pores. As a result, higher dosage of OMMT micro-particles is needed to efficiently fill the space of capillary pores within the cement mortars. Meanwhile, OMMT micro-particles can be more easily stirred in cement slurry and are more difficult to form clusters with cement grains when the water/cement ratio is higher. Consequently, the optimal dosage of OMMT micro-particles depends on the water/cement ratio of cement mortars in a mix design. From Fig. 15, it is also found that the optimal dosages of OMMT micro-particles for a lower coefficient of permeability of cement mortars are in the range of 0.25–0.75%. Therefore, it can be said that the strengths and permeability of cement mortars can be much improved if appropriate amount of OMMT micro-particles, for example 0.25–0.75% for the cement mortars we studied here, is used and random dispersion of OMMT micro-particles around capillary pores can be achieved after complete mixing.

4. Conclusions

The OMMT micro-particles are hydrophobic and can be utilized as reinforcements to improve the strengths and permeability of cement mortars. From SEM micrographs and EDS analysis, it is found that the OMMT micro-particles could act as diffusion barriers around capillary pores for cement mortars reinforced with a lower dosage of OMMT micro-particle. However, clusters of OMMT micro-particles are more likely to occur and can be observed from SEM micrographs when the dosage of OMMT micro-particles is larger than 1%. Meanwhile, MIP measurements indicate that the pore size distribution of cement mortars is significantly influenced by the introduction of OMMT micro-particles. For cement mortars reinforced with a lower dosage of OMMT micro-particles, the total volume of accessed pore is decreased, the volume of larger pores, however, is slightly increased but the pore size distribution of smaller pores is less affected. At the same time, the accessible pore volume of intermediate pores, larger than 0.01 μm but less than 0.2 μm, is significantly reduced due to the obstruction of OMMT micro-particles around capillary pores.

Both the compressive and flexural strengths of cement mortars increase initially and then decrease dramatically after reaching a peak value as the dosage of OMMT micro-particles is increased. Reversely, the coefficients of permeability of cement mortars decrease at first and then increase rapidly after reaching a minimum. The increase of compressive strengths of cement mortars could be up to 30–40% but the increase of flexural strengths is less than 10%; their coefficients of permeability might be 10–100 times lower. It is known that compressive strengths are primarily controlled by the total porosity in cement mortars while flexural strengths are affected by the critical pore size as well as the total porosity. For cement mortars with a lower dosage of OMMT micro-particles, the total porosity is reduced but the critical pore size is increased. As expected, the increase of compressive strengths is higher than that of flexural strengths.

The optimal dosages of OMMT micro-particles for the improvements of strengths and permeability of cement mortars depend on the water/cement ratio of a mix design. For example, the optimal dosages of OMMT micro-particles for compressive strengths of cement mortars are less than 0.25% when w/c=0.4, 0.25–0.5% when w/c=0.485 and 0.5–0.75% when w/c=0.55. Thus, it can be said that the optimal dosage of OMMT micro-particles approximately increases with the water/cement ratio in a mix design. When both strengths and durability are sought, the optimal dosage of OMMT micro-particles is found to be less than 1% and OMMT micro-particles should be randomly distributed around capillary pores in cement mortars after complete mixing.

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