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The properties of hydrophobic concrete prepared by biomimetic mineralization method

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Abstract. In this study, the calcium hydroxide, an inherent product of cement hydration, was treated using biomimetic carbonation method of incorporating stearic acid to generate the hydrophobic calcium carbonate on concrete surface. Carbonation reaction was carried out at various CO_2 pressure and temperatures and utilizing the Scanning Electron Microscope (SEM), chloride-ion penetration test apparatus, and compression test machine to investigate the hydrophobicity, durability, and mechanical properties of the synthesized products. Experimental results indicate that the calcium stearate may change the surface property of concrete from hydrophilicity to hydrophobicity. Increasing reaction temperature can change the particles from irregular shapes to needle-rod structures with increased shear stress and thus favorable to hydrophobicity and microhardness. The contact angle against water for the concrete surface was found to increase with increasing CO_2 pressure and temperature, and reached to an optimum value at around 90℃. The maximum static water contact angle of 128.7 degree was obtained at the CO_2 pressure of 2 atm and temperature of 90℃ . It was also found that biomimetic carbonation increased the permeability, acid resistance and chloride-ion permeability of the concrete material. These unique results demonstrate that the needle-rod structures of $CaCO_3$ synthetized on concrete surface could enhance hydrophobicity, durability, and mechanical properties of concrete.

Keywords: concrete; biomimetic carbonation; hydrophobicity; durability; strength

1. Introduction

Concrete is the most important and common construction materials used in civil engineering projects. It is essential that concrete is a durable material, that should withstand the conditions for which it has been designed, without deterioration, over a period of years (Deilami 2017). Devi (2018) indicated that durability is the property of concrete, which has the ability to withstand weathering action, chemical attack, abrasion or any other process of deterioration.

Service life of concrete depends mainly on its durability, i.e,. the ability to resist physical effects (freezing and thawing, abrasion, erosion, drying shrinkage), chemical attacks (leaching and efflorescence, sulfate attack, acidic solution), weathering, and attack by natural or industrial liquids and gases. Li *et al.* (2017), Li *et al.* (2018) have advised that the permeability of concrete is believed as the key property related to the serviceability and durability of concrete structures (e.g., bridges, hydraulic structures and marine structures) subjected to aggressive environments.

To improve the permeability of concrete, one of effective methods is waterproofing treatment which is adequate to make a hydrophobicity surface on concrete. Hydrophobic treatment can prevent wetting of the concrete's porous structure and in turn provides the self-cleaning ability that was called the "lotus effect" (Zhang *et al.* 2016). From the previous studies (Liu and Hansen 2016, Arabzadeh 2017, Sadowski and Stefaniuk 2018), making a hydrophobic surface has two requirements: rough surface and low surface energy. There are two methods could be produced a hydrophobic surface. First mothed, make a rough surface with a hydrophobic material, and second method is chemically modified the surface or coating a hydrophobic material upon it. To chemically modify the surface with a hydrophobic coating has several ways including sol-gel (Mishchenko 2012), dip coating (Ebert and Bhushan 2012), electrochemical (Zhang *et al.* 2004), and chemical or physical vapor deposition (Lau *et al.* 2003, Hosono *et al.* 2005).

In addition, the hydrophobicity of concrete can be increased by forming a film of calcium carbonate to block the pores and reducing the permeability of the surface layer. $Ca(OH)_2$ can also be fixed by treatment with diluted water-glass. Calcium carbonate is then formed and filled the pores (Amidi and Wang 2015, Lertwattanaruk 2018). Treatment with magnesium fluorosilicate is also possible (Jia 2015, Pana 2018). Concrete carbonation is a process in which carbon dioxide reacts with calcium hydroxide ($Ca(OH)_2$) in the cement matrix to form calcium carbonate ($CaCO_3$) (Park 2008). Preparation of $CaCO_3$ in the presence of all kinds of organic substrate using soluble carbonate and calcium salts as initial materials has been reported by Wada (2004), Tong

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(2004), Grassmann and Löbmann (2004). It indicated that the organic substrate induced the nucleation and growth of $CaCO_3$, but does not change the surface property of $CaCO_3$. Keum *et al.* (2002) prepared hydrophobic $CaCO_3$ particles by mineralization with sodium trisilanolate in methanol solution. Chen *et al.* (2010) have reported carbonation of $Ca(OH)_2$ to synthesize cubic $CaCO_3$ using dodecanoic acid as modifier. Several organic additives used for synthesizing hydrophobic $CaCO_3$ via carbonation of $Ca(OH)_2$ include oleic acid (Wang and Sheng 2006), octadecyl dihydrogen phosphate (Wang and Xiao 2006), sodium oleate (Sheng 2006), stearic acid (Wang and Sheng 2007), and dodecanoic acid (Wang 2010).

In this research, the hydrophobic $CaCO_3$ nanoparticles were synthesized in situ in the presence of stearic acid by carbonating route via, mimicking the essential functions of bio-mineralization. The level of temperature and pressurized CO_2 of carbonation reaction was found to have a great effect on the morphology of $CaCO_3$ and thus the hydrophobic of the concrete surface. Furthermore, the carbonation and mineralization could not only induce the nucleation and growth of $CaCO_3$ nanoparticle but also improve the surface hydrophobicity, durability, and the compressive strength of the concrete.

2. Experimental procedure

2.1 Testing program

A laboratory study was performed to generate a hydrophobic concrete surface via a carbonation route using sodium stearate surface. Carbonation reaction was carried out with varied temperatures and CO_2 pressure by an autoclave to investigate the hydrophobicity and morphology of the calcium carbonate in this study. Three groups of concrete cylinder specimens were prepared for surface carbonation treatment and the designated testing. The first group was control specimens that cured under room temperature (25℃) and moist condition. The second group was taken for conventional carbonation reaction done in the autoclave at CO_2 pressure of 2 atm (atmosphere), and the third group was additionally added in the autoclave an organic solution which was taking 1:1 molar ratio of stearic acid and sodium hydroxide in 400ml of deionized water. The specimens were tested or measured with Scanning Electron Microscope (SEM), chloride-ion penetration apparatus, and compression test machine for evaluating the hydrophobic properties, micro structure, chloride-ion permeability, acid resistivity, and the strength of the resulting specimens.

2.2 Cast of concrete specimens

The concrete used for casting cylinder specimens had a material mixture that including ordinary portland cement, water, sand, and coarse aggregate with the mix proportion (by weight) of 2:1.2:6.1:6.8 and a water cement ratio of 0.6. Each mixture was mixed in accordance with ASTM C192 (2016). Two sizes of cylinder were prepared for tests, one is Φ100×200 mm in size cast for compressive strength, rapid chloride-ion penetration, and acid resistance test, the other is Φ150×300 mm in size cast for permeability test. The cylinder specimens were demolded after 24 hours and placed in a 100% humidity curing room for one day. These specimens were then taken for two methods of carbonation reaction treatment.

2.3 Carbonation reaction treatments of concrete specimens

Two methods of carbonation reaction treatment were adopted as follows:

2.3.1 Conventional carbonation reaction treatment method

In this method, the concrete cylinders were carried out carbonation reaction treatment in an autoclave (Autoclave Engineers, V=500 cm^3). The autoclave was sealed and pressurized with CO_2 to a pressure of 2 atm. The carbonation reaction was carried out for a period of 72 hours. After this the CO_2 gas was vented off, the cylinders were oven dried at 40℃ for one day and then cured under room temperature for 28 days preparing for tests. These specimens are referred as CC.

2.3.2 Biomimetic synthesis of CaCO3 nanoparticle using carbonation method

This method is a biomimetic synthesis of an inorganic-organic composite that induce the nucleation and growth of $CaCO_3$ particle under the organic substrate in aqueous solution. The carbonation was done in the autoclave at CO_2 pressure of 0.5, 2, and 5 atm. The organic solution was prepared by taking stearic acid and sodium hydroxide in deionized water and was filled so as to cover the cylinders in the autoclave. The autoclave was sealed and pressurized with CO_2. The carbonation reaction was carried out at 5 temperature levels of 25, 40, 90, 120 and 150℃ for a period of 24 hours. The After this the cylinders were taken out and dried at 40℃ for one day and then cured under room temperature for 28 days preparing for tests. The carbonation reaction treatments for the specimens are summarized in Table 1, in which B refers to biomimetic synthesis and C means the carbonation condition. For example, BC 0.5-20 represents the biomimetic carbonation reaction under CO_2 pressure of 0.5 atm with the temperature of 25℃.

Table 1 Carbonation treatments for the specimens and the measured compressive strength

Specimen No.	CO_2 pressure (atm)	Reaction temperature (℃)	compressive strength (MPa)
NC	0	25*	31.1±1.51
CC	2	25	32.4±1.21
BCa-25	0.5	25	31.6±1.07
BC2-40	2	40	35.5±0.68
BC2-90	2	90	39.4±0.64
BC2-120	2	120	39.1±0.94
BC2-150	2	150	38.0±0.88
BC5-90	5	90	39.2±0.93

*Room temperature

2.4 Preparation of organic substrates

The organic solution was prepared by taking 1:1 mole ratio (0.01 moles) of stearic acid ($C_{18}H_{36}O_2$) and sodium hydroxide in 400ml of deionized water. Having been stirred at 95℃ for 6mins, a saponification solution ($C_{17}H_{35}COONa$) was obtained to be used as organic substrate.

2.5 Testing of specimens

After carbonation reaction treatments and 28 days curing, the specimens, including the non-carbonated control cylinders that referred as NC, were prepared for various tests. The compression test was carried out (three specimens each for testing) based on ASTM C39 (2016). The microhardness test was conducted in accordance with ASTM E384 (2017) using a microindentation tester (Shimazu Micro Hardness Tester HMV-2). According to the code, the Vickers hardness number (HV) is calculated as follows

$$HV = 1.8544 \times \frac{P}{d^2} \text{ (MPa)} \quad (1)$$

where, P=force (N), d=mean diagonal length of the indentation (mm).

To determine the morphology and particle size of the carbonated products, scanning electron microscope (SEM) measurements were carried out on Hitachi S4800-I Field Emission scanning electron microscope. The static water contact angles of the specimens were measured using FTA 1000 contact angle goniometer by the sessile drop method using a micro syringe at 25℃. The resistance of the concrete to penetration of the chloride-ions, measured in terms of the charge passed through the concrete, was determined on the carbonation reaction treated disk (Φ100×50 mm) cut from the cylinder (Φ100×200 mm) in accordance with ASTM C1202 (2017). The water permeability of concrete was measured using a conventional water permeability apparatus subjected to a water pressure of 2 MPa by determining the flow through the concrete specimen (Φ150×50 mm). To measure the acid resistance of concrete the specimens were immersed in an acidic solution of three pH levels (2.6, 4.6 and 6.6) for 24 hours and determined the weight loss of the specimens before and after test.

3. Results and discussion

3.1 Hydrophobic surface properties of biomimetic synthesized $CaCO_3$ particles

Concrete is inherently a hydrophilic material. This water permeable property can be improved via a carbonation route using sodium stearate in this experiment to generate an effective hydrophobic concrete surface consisting of calcium carbonate nanoparticle.

The hydrophobic function is often interpreted as static water contact angle (WCA) and is sometimes referred to as "lotus effect" (Zhang 2016). Zhao (2018) have showed that the WCA depends on several factors, such as surface energy, surface roughness, and the cleanliness. If the liquid molecules are strongly attracted to the solid molecules then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0°. Generally, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic. A surface is called super-hydrophobic, only and if only, the measured contact angle on it is equal to or greater than 150 degrees. 9. The static water contact angle can be equal to or greater than 90 degrees but it is only smaller than 180 degrees.

To demonstrate the lotus effect, hydrophobicity as the basis for self-cleaning mechanism, the organic interaction characteristic of concrete surface was measured by contact angle. The organic additive changes the property of concrete material in situ, Table 2 shows the measured WCA of the concrete surfaces obtained at different carbonation reaction temperatures and pressurized CO_2 pressure. It is seen from Table 2 that at room temperature (25℃) the contact angle against the hydrophobic concrete surface was almost zero, similar as those of the specimen NC (control) and CC(conventional carbonation). The contact angle increased when the CO_2 pressure increased and the temperature enhanced. Under similar CO_2 pressure of 2 atm, as shown in Fig. 1, the WCA increased gradually to the maximum value of 128.7℃ for the temperature of 90℃. This reveals that the temperature increases the efficient interaction of stearate molecules and Ca^{2+} and CO_3^{2-} inducing hydrophobic calcite hence an increment in the WCA. However, further increase in temperature caused slight decrease in the WCA and remained even constant

Table 2 Measured static water contact angle values of concrete surface

Specimen No.	Carbonation conditions			WCA* (°)
	Method	CO_2 (atm)	Temp. (℃)	
NC	None	0	25	0
CC	Conventional	2	25	0
BCa5-25	Biomimetic	0.5	25	44.7 (42.1, 44.7, 45.1, 44.8, 46.8)
BC2-40	Biomimetic	2	40	84.7 (86.3, 88.8, 84.1, 78.6, 85.5)
BC2-90	Biomimetic	2	90	128.7 (132.0, 126.7, 130.7, 127.8, 126.3)
BC2-120	Biomimetic	2	120	119.4 (120.1, 119.4, 118.8, 120.2, 118.7)
BC2-150	Biomimetic	2	150	118.8 (119.9, 117.9, 118.3, 121.2, 116.9)
BC5-90	Biomimetic	5	90	129.5 (122.8, 134.8, 137.1, 124.7, 128.0)

*WCA: Static water contact angle, average value.

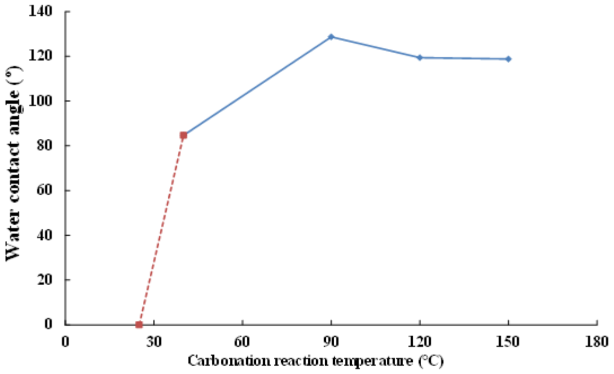
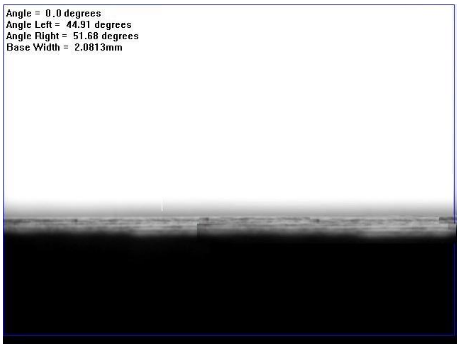


Fig. 1 Static water contact angle values of concrete surface at various temperatures

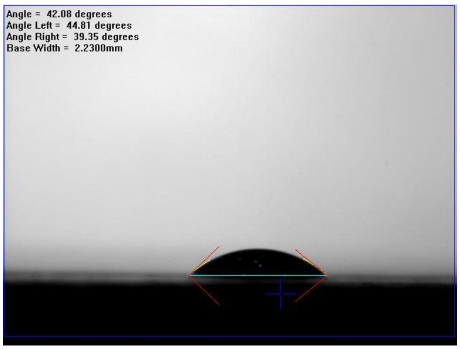
after 90°C. This indicates that the higher temperature ranged around 90°C is the most favorable selection for the carbonation reaction treatment to generate a hydrophobic calcium carbonate. Fig. 2 displays the WCA of the concrete specimens at various temperatures. In addition, when the CO_2 pressure increased to 5 atm, the WCA reached to 129.5°, it is just an insignificant increase of WCA, as compared with 128.7° for the BC2-90 specimen. Consequently, the CO_2 pressure of 2 atm and temperature of around 90°C can be adopted as an optimal carbonation reaction treatment.

3.2 Effect of carbonation reaction on the compressive strength of concrete

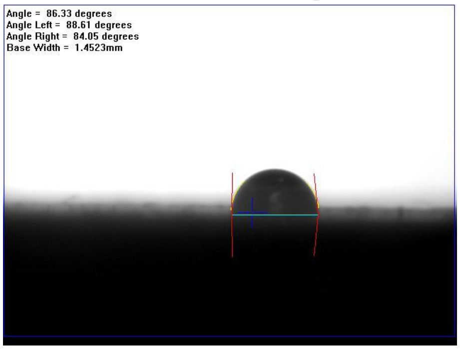
The compressive strength of the cylinder specimens was tested at the age of 28 day. The test results are summarized in Table 1 and Fig. 3. It shows that the control specimen (NC) presents an average strength of 31.1 MPa. It is lower than those of the concrete treated with conventional carbonation (CC: 32.4 MPa) and biomimetic carbonation at 40°C (BC2-40: 35.5 MPa), while a significant strength increase is observed on the concrete treated with biomimetic carbonation at higher temperature of 90 and 120°C (BC2-90: 39.4 MPa, BC2-120: 39.1 MPa). The



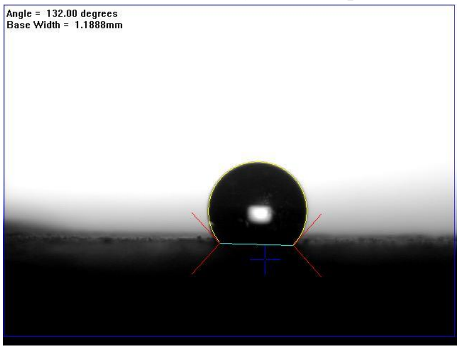
(a) 25°C and 0atm (NC specimen)



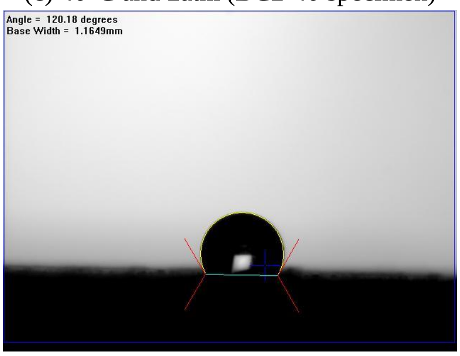
(b) 25°C and 0.5atm (BCa-25 specimen)



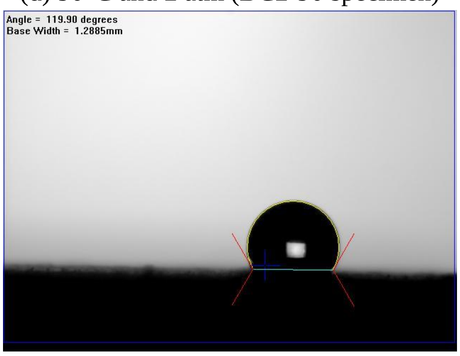
(c) 40°C and 2atm (BC2-40 specimen)



(d) 90°C and 2 atm (BC2-90 specimen)



(e) 120°C and 2 atm (BC2-120 specimen)



(f) 150°C and 2 atm (BC2-150 specimen)

Fig. 2 Static water contact angle images of the concrete samples with various carbonation treatments

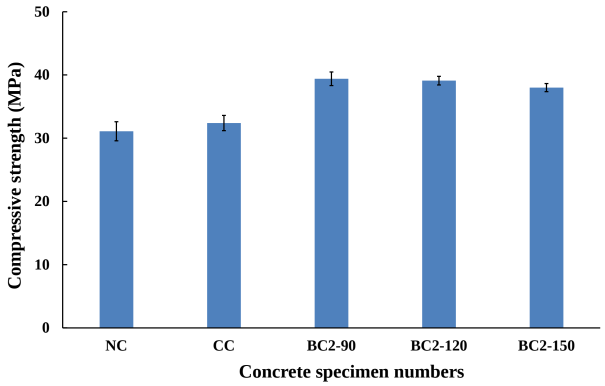


Fig. 3 Compressive strength of concrete cylinders with various carbonation treatments

reason for increased strength of concrete treated with biomimetic mineralization is due to the high temperature and pressure that enhance the hydration of water and cement. These results indicate that both carbonation treatment methods can improve the strength of concrete, especially; an obvious strength increase may be attained for the concrete treated with biomimetic carbonation method at high temperature of around 90℃.

3.3 Carbonation reaction induced microhardness improvement of concrete

The microhardness test was principally measured on the cement matrix of concrete surface. Table 3 lists the measured results of microhardness value (Vickers hardness number, HV) for all specimens. It is seen that the control specimen (NC) without carbonation treatment presents the lowest HV value of 11.6 MPa. Both carbonation treatment methods can improve the microhardness of concrete, and furthermore, the biomimetic carbonation at higher temperature exhibits a favorable effect on the hardness of concrete. This can be observed from Fig. 4 that the microhardness value first increases and then decreases with temperature; after 90℃ there are no further increase. To interpret the facts of the enhanced microhardness for the specimens BC2-40 and BC2-90 treated with biomimetic carbonation, series SEM measurements were carried out on the specimens. Fig. 5 illustrates the SEM images of the carbonated specimens, which presents differences in particle morphology and obviously depending on carbonation reaction temperature. At 25℃ (CC specimen) the product has irregular morphology mostly in the form of plate and consists scarcely of needle $CaCO_3$. At temperature of 40℃ and 90℃ these irregular particles transform to needle-rod structures of $CaCO_3$ mostly with a mean particle length of 0.5-1 μm, which causes increased calcite fiber mineral filler for bridging between cement particles, and thus increasing micro hardness of the interface. Calcium carbonate on the concrete surface can be rendered water-repellent by the templating method mainly due to changes in its crystalline form, independent of chemical composition. The principle of the template method is that sodium stearate adsorbs calcium ions when calcium hydroxide reacts with carbon dioxide to carbonize. This

Table 3 Measured results of the microhardness value of concrete specimens

Specimen No.	Carbonation conditions: Method	CO_2 (atm)	Temp. (℃)	Vickers hardness number, HV (MPa)
NC	None	0	25	11.6 (11.2, 10.8, 12.8)
CC	Conventional	2	25	12.1 (11.6, 12.3, 12.4)
BC0.5-25	Biomimetic	0.5	25	12.8 (13.2,12.7,12.5)
BC2-40	Biomimetic	2	40	25.6 (25.9, 25.1, 25.8)
BC2-90	Biomimetic	2	90	31.9 (32.1, 31.7, 31.9)
BC2-120	Biomimetic	2	120	29.3 (28.9, 29.5, 29.6)
BC5-150	Biomimetic	5	150	27.7 (27.1, 28.4, 27.7)

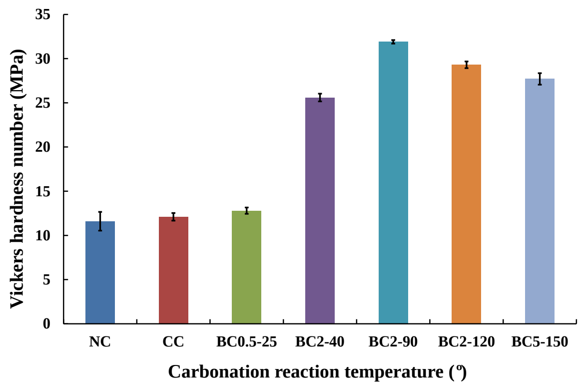


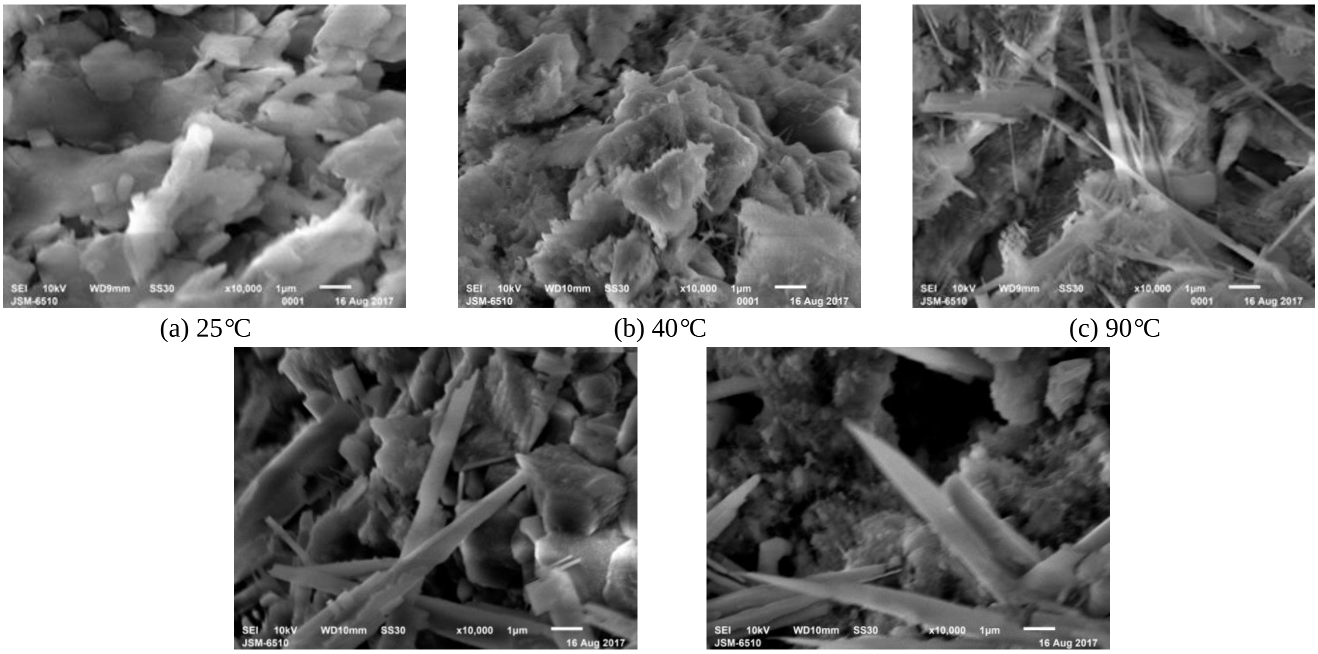
Fig. 4 Microhardness of concrete obtained at different carbonation reaction temperatures with and without sodium stearate

calcium carbonate crystallizes only in the long-chain direction of sodium stearate to form long needle-rod calcium carbonate. It has a hydrophobic effect on the concrete surface.

At higher temperatures of 120℃ the needle-rod structures transforms to aggregate particles (plate-like), resulting in a less microhardness value. In general, plate-like structures are easy to stack up, and the structure is dense and compact, and resulting in higher microhardness.

3.4 Effect of carbonation reaction on the durability enhancement of concrete

According to ACI Committee 201, durability of concrete is defined as the ability to resist weathering action, chemical attack, abrasion or other process of deterioration. So the control factors responsible for lack of durability of concrete are adequate to be concluded as water, permeability and harmful ion, such as acids. To evaluate the durability of concrete after carbonation reaction treatment, three kinds of test including water permeability test, rapid chloride ion permeability test, and acid resistance test, were adopted for measuring the water permeability, the resistance to the chloride ion penetration, and the acid resistivity of concrete.



(a) 25℃ (b) 40℃ (c) 90℃

(d) 120℃ (e) 150℃

Fig. 5 SEM images of the carbonated specimens at various temperatures

All results are summarized and discussed as follow:

3.4.1 Water permeability of concrete

Experiments were performed using water permeability apparatus on cylinder specimen (Φ150×50 mm) with 2.0 MPa pressure for 3 hours. The water permeability was calculated with following formula

$$\text{Water permeability} = \frac{m2-m1}{m1} \times 100\% \qquad (2)$$

where, $m1$=initial weight of specimen (g), and $m2$=specimen weight (g) after test.

Table 4 shows the measured water permeability of the concrete specimens. It is seen that the conventional carbonation cannot improve the water permeability of normal concrete. The water permeability will be significantly improved when the concrete was treated with biomimetic carbonation at higher temperature, in which around 90℃ is the best condition, the water permeability of concrete may be decreased from around 0.89% to around 0.25%. This situation can be also observed on Fig. 6, which shows the correlation between WCA and the water permeability of concrete. It is seen from Fig. 6 that the water permeability of concrete decreases with the increase of static water contact angle or the hydrophobicity of concrete.

Table 4 Measured results of the water permeability of concrete specimens

Specimen No.	WCA (°)	Water pressure (MPa)	Test time (min.)	Water permeability (%)
NC	0			0.89 (0.88, 0.88, 0.90)
CC	0			0.86 (0.87, 0.87, 0.85)
BCa25-25	44.7	2	180	0.73 (0.73, 0.72, 0.74)
BC2-40	84.7			0.25 (0.25, 0.25, 0.26)
BC2-90	128.7			0.23 (0.22, 0.22, 0.24)

3.4.2 Resistance of concrete to the penetration of chloride ions

Experiment of the resistance of concrete to penetration of the chloride ions, measured in terms of the electric charge passed through the concrete in coulombs, was determined on two disksΦ100×50 mm in size cut from the top portion of the cylinder specimen (Φ100×200 mm). Table 5 lists the measured results of all specimens and their corresponding static water contact angles of concrete surface. It is seen that the CC specimens (conventional carbonation treatment) exhibited low resistance to the penetration of the chloride-ion (high values of the total charge passed of 4012 coulombs) similar as that of NC specimens (the total charge passed of 4995 coulombs). On the other hand, when the concrete was treated with biomimetic carbonation, such as specimens BC0.5-25, BC2-40 and BC2-90, they all showed higher resistance to the chloride-ion penetration with relatively lower total charge passed of 1204, 766, and 33 coulombs, respectively. These results indicate the favorable effects of biomimetic carbonation treatment on the durability of concrete, especially for the specimen BC2-90 (carbonation reaction at temperature of 90℃).

Fig. 7 shows the correlation between WCA and the total charge passed of concrete. The curve is found to have the similar tendency as that of the Fig. 6 of WCA vs. water permeability of concrete. Consequently, it can be concluded that the total charge passed of concrete decrease with the

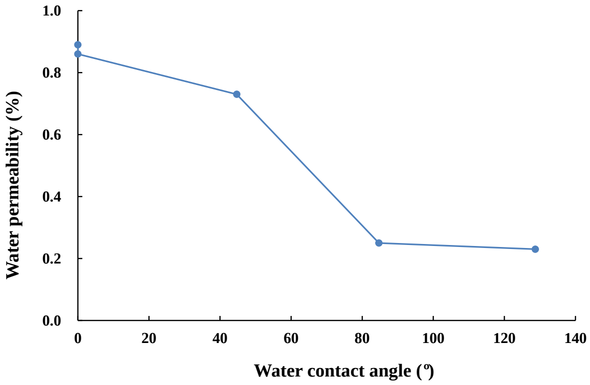


Fig. 6 Relationship between static water contact angle and water permeability of concrete

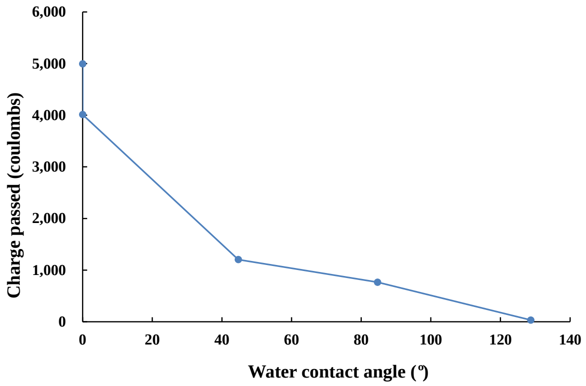


Fig. 7 Relationship between static water contact angle and charge passed of concrete

increase of static water contact angle or the hydrophobicity of concrete.

3.4.3 Acid resistivity of concrete

Experiment of the acid resistivity of concrete was performed on the cylinder specimen (Φ100×50mm) that immersed in acidic solution of 3 pH levels (2.6, 4.6, and 6.6) for 24 hours and then calculated the loss rate of specimen weight as follows for evaluating its acid resistivity

$$\text{Wight loss} = \frac{w1-w2}{w1} \times 100\% \qquad (3)$$

where, w_1=initial weight of specimen (g), and w_2=specimen weights (g) after test.

Table 6 gives the measured results of all specimens and their corresponding static water contact angles of concrete. It is found that for each pH level of solution the specimens NC and CC exhibited relatively larger weight loss value than those of the specimen BC0.5-25, BC2-40, and BC2-90. Among them the specimen BC2-90 presented the lowest value, indicating to have best acid resistivity. In addition, the weight loss of each individual specimen varied with different pH value of solution, such as specimen NC exhibited the weight loss value of 1.67%, 0.39%, and 0.11% for the corresponding pH value of 2.6, 0.6, and 6.6, respectively. These situations can be also observed on Fig. 8. It is seen that the weight loss value for each specimen

Table 5 Measured results of the resistance to chloride penetration of concrete specimens

Specimen No.	WCA (°)	Total charge passed (coulombs)	Chloride Ion Penetrability*	Vickers hardness number, HV (MPa)
NC	0	4995 (4981, 5006, 4998)	High	11.6
CC	0	4012 (4020, 4031, 3985)	High	12.1
BCa25-25	44.7	1204 (1212, 1195, 1205)	Low	12.8
BC2-40	84.7	766 (769, 773, 756)	Very Low	25.6
BC2-90	128.7	33.0 (31.9, 34.4, 32.7)	Negligible	31.9

*Chloride Ion Penetrability based on charge passed (ASTM C1202 2017):
High: >4000; Moderate: 2000~4000; Low: 1000~2000; Very low: 100~1000; Negligible: <100.

Table 6 Measured results of the acid resistivity of concrete specimens

Specimen No.	Solution pH value	Test time (hr.)	Weight loss ratios (%)
NC			1.674 (1.674, 1.674, 1.675)
CC			1.112 (1.109, 1.111, 1.116)
BCa25-25	2.6	24	0.774 (0.775, 0.773, 0.774)
BC2-40			0.610 (0.608, 0.611, 0.612)
BC2-90			0.433 (0.428, 0.433, 0.439)
NC			0.386 (0.387, 0.378, 0.394)
CC			0.314 (0.311, 0.309, 0.322)
BCa25-25	4.6	24	0.152 (0.159, 0.147, 0.151)
BC2-40			0.119 (0.122, 0.122, 0.112)
BC2-90			0.082 (0.085, 0.080, 0.081)
NC			0.112 (0.111, 0.112, 0.113)
CC			0.080 (0.080, 0.081, 0.079)
BCa25-25	6.6	24	0.032 (0.032, 0.029, 0.035)
BC2-40			0.020 (0.019, 0.018, 0.022)
BC2-90			0.009 (0.009, 0.008, 0.010)

increases with the decrease of pH value. And the specimens undertaken the solution of strong acid (pH=2.6) exhibit obvious higher weight loss values, except the specimen BC2-90 with biomimetic carbonation treatment. These results indicated that the concrete treated with adequate biomimetic carbonation may possess inherent acid resistivity.

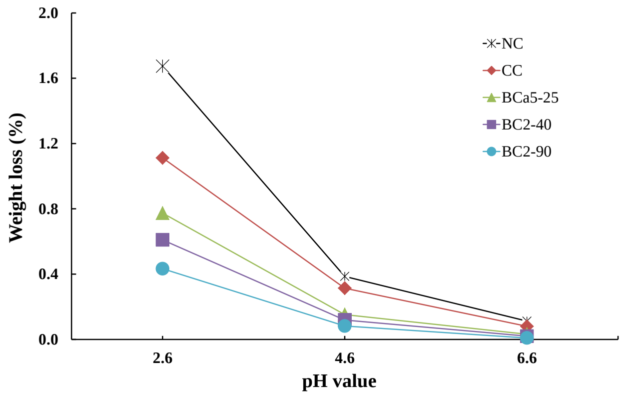


Fig. 8 Weight loss of concrete under various pH value of solution

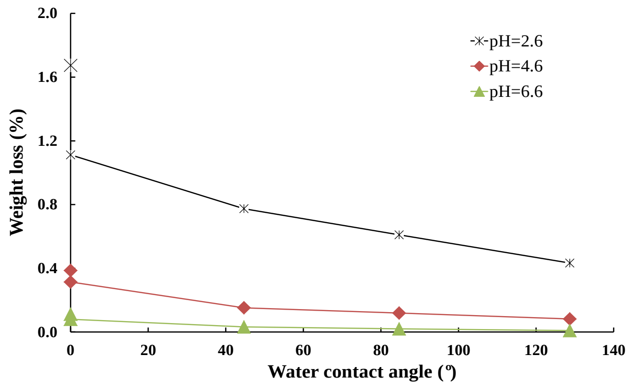


Fig. 9 Relationship between static water contact angle and Weight loss of concrete

On the other hand, observing the correlation between static water contact angle and the weight loss of concrete as shown in Fig. 9. It can be found that the weight loss value of concrete decrease with the increase of static water contact angle or the hydrophobicity of concrete.

3.4.4 Effect of biomimetic carbonation treatment on the durability of concrete

The above test results have verified the fact that concrete treated with biomimetic carbonation may improve its hydrophobic ability owing to producing the needle-rod structures of $CaCO_3$ nanoparticle, which causes increased calcite fiber mineral filler for bridging between cement particles. This bridging effect of the calcite fiber mineral may result in an increased density, and thus enhance the micro hardness of concrete.

Basically, the measured static water contact angle (WCA) of concrete is adopted to express the hydrophobicity of concrete; the microhardness of concrete may then have well relationship with the WCA, as shown in Fig. 10 plotted from Table 2 and Table 3. It shows that the microhardness of concrete increases with the increase of WCA, namely, the hydrophobicity of concrete. Comparing the curve of Fig. 10 with those of Fig. 6, 7, and 9, a similar curve trend can be found among them that increased static water contact angle leads to the equivalent decreases of water permeability, total charge passed, and weight loss of concrete. Since these

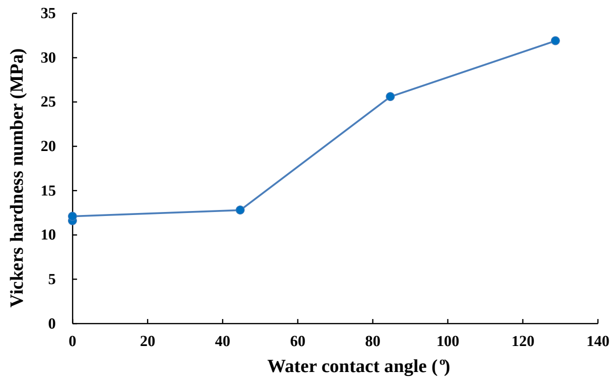


Fig. 10 Relationship between static water contact angle and microhardness of concrete

items are the control factors of durability, it is adequately concluded that the concrete treated with biomimetic carbonation may obviously improve its hydrophobicity, and in turn enhance the durability characteristics.

4. Conclusions

Experiments results of the concrete treated with biomimetic carbonation carried out at various CO_2 pressure and temperature to investigate its hydrophobicity, durability, and mechanical properties are presented. On the basis of results obtained in this research, the following conclusion can be drawn:

- The calcium hydroxide produced from cement hydration can be treated with stearic acid to generate the hydrophobic calcium carbonate on concrete surface, and thus enhances its hydrophobicity.
- The most appropriate temperature and the pressurized CO_2 pressure for the biomimetic carbonation reaction are suggested as around 90℃ and 2 atm, respectively.
- Concrete with water cement ratio of 0.6 treated with the optimal biomimetic carbonation can improve the compressive strength and microhardness for around 26% and 65%, respectively.
- Based on the test results that increased microhardness of concrete (also the static water contact angle) leads to the decrease of water permeability, total charge passed, and weight loss of concrete, it is concluded that the concrete treated with biomimetic carbonation may improve its hydrophobicity, and in turn enhance the durability.

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