Int. J. Electrochem. Sci., 12 **(2017)** 11692 – 11700, doi: 10.20964/2017.12.38

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Impedance Spectroscopy Study of the Compressive strength of Concrete

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Received: 27 August 2017 / *Accepted:* 23 September 2017 / *Published:* 12 November 2017

The compactness of cementitious materials is closely related to their mechanical properties and durability. In addition to compressive strength testing, electrochemical impedance spectroscopy (EIS) was applied to measure mortars with different cement contents. The relationships between the compressive strength and EIS results are also discussed. The results suggest that the compressive strength of the samples increased with the impedance and phase angle at low frequency. In particular, most of the compressive strength almost linearly increased with the phase angle when the frequency was lower than 10 Hz. Consequently, compared with the impedance values, the phase angle at low frequency is more suitable for assessing the compressive strength of concrete.

Keywords: Concrete; Compressive strength; EIS; Compactness of concrete

1. INTRODUCTION

Concrete compactness is closely related to the compressive strength, water permeability and the diffusion of aggressive ions in the concrete [1–5]. It is important to assess the compactness of concrete. However, traditional measurements of the compactness of concrete are destructive, which restricts their applications in service structures. Electrochemical impedance spectroscopy (EIS) is a non-destructive method that is widely used to estimate the corrosion of reinforcing steel in concrete [6–12], the carbonation of concrete [13] and the permeation of corrosive ions in cementitious materials [14]. Yang [15] applied EIS to study the effect of surface-sulfonated polystyrene microspheres on the crack resistance of carbon microfiber-reinforced Portland cement mortar. Using an equivalent circuit to represent the resistances of the mortar matrix and that of the continuously and discontinuously connected pores or cracks in the mortar, the authors noticed that the added surface-sulfonated polystyrene microspheres retarded the initiation of unrecoverable microcracks and slowed down the propagation of microcracks under uniaxial compression loading. Montemor [16] also used EIS to study the effect of fly ash on the corrosion behavior of rebar in concrete and their results showed that the fly ash increased the resistivity of concrete and decreased the corrosion rate of rebar. Marriaga [17] investigated the effect of the interfacial transition zone on the transport related properties of Portland cement mortars by EIS and an equivalent circuit. The authors reported that rapid chloride penetrability is related principally to conductive pores, but is also related to the total impedance of the non-conductive pores. This brief review indicates the importance of equivalent circuits in studying concrete properties [13–15, 17]. In the present study, the compactness of cementitious materials is studied by the impedance value and phase angle in the EIS tests. The results suggest that the phase angle is an index parameter of the compactness of cementitious materials.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Mortars were prepared with ordinary Portland cement (P.O 42.5), slag (S95 grad) and the HLC polycarboxylate superplasticizer (HLCPS), produced by the Nanjing Hydraulic Research Institute. For preparing the mortars with different compactness values, different cement contents of 12.5%, 15%, 17.5% and 20% by weight of the total solid material were chosen. The slag contents and HLCPS are fixed at 10.5% (by weight of sand) and 0.438% (by weight of cement and slag), respectively. The mixture proportions for mortar samples are listed in Table 1.

Table 1. Mixture proportions for cementitious materials with different cement contents (g/dm^{-3}).

	Sand	Cement	Content of cement	Slag	HLCPS	Water
A1	1500	236.8	12.5%	157.5	1.73	255.7
A2	1500	292.5	15%	157.5	1.97	263.3
A3	1500	351.6	17.5%	157.5	2.23	271.2
A4	1500	414.4	20%	157.5	2.51	279.7

2.2 Experiments

Cubic specimens with a side length of 70.7 mm were prepared and stored in air at room temperature for 24 h. Then, the samples were demolded and cured in a chamber with T = 20 ± 2 °C and RH = 95 ± 3%. After curing for 7, 14 and 28 d, using a universal testing machine at a rate of 0.3 mm/min, compressive strength testing is conducted with the cubic specimen with the cubic mortar specimen. Each experiment was performed in triplicate and each time a new sample was used. An AISI304 stainless steel rod (diameter of 10 mm) was embedded in the middle of the cylindrical mold with a size of Φ40 × 60 mm for electrochemical testing. After curing for 24 h, the cylindrical mortar samples were also removed from the molds and immersed in clean tap water. After immersion for 7, 14 and 28 d, the EIS tests were performed with a platinum electrode as the counter electrode and a saturated calomel electrode as the reference electrode, respectively. By applying an AC disturbance signal of 10 mV on the stainless steel electrode at the open circuit potential, EIS measurements were carried out at a frequency range of 10^5 to 10^{-2} Hz.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

After curing for the design time, the compressive strengths of the samples with different cement contents were measured. The compressive strengths of the cementitious material increases with increasing cement content (Figure 1). Additionally, for comparing the compressive strength results, the values of samples at different curing times are plotted together (Figure 2). It is easy to notice that the compressive strength of the samples linearly increases with the cement content. This is consistent with the results of Consoli [18]. After studying the mechanical properties of the silty soil treated with cement, the authors reported that the compressive strength of the cement-soil linearly increased with increasing cement content. When cement is mixed with sand and slag, the calcium silicate ($3CaO{\cdot}SiO_2$), dicalcium silicate ($2CaO{\cdot}SiO_2$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) and calcium ferrite aluminate ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$) in cement separately react as follows [14]:

$$2(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \quad (2)$$

$$3CaO.Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO.Al_2O_3.Ca(OH)_2.12H_2O \quad (3)$$

$$4CaO.Al_2O_3.\ Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO.\ Al_2O_3.\ Fe_2O_3.12H_2O \quad (4)$$

The reaction products, $3CaO{\cdot}2SiO_2{\cdot}3H_2O$ (*C–S–H*) and $3CaO{\cdot}Al_2O_3{\cdot}Ca(OH)_2{\cdot}12H_2O$ (*C–A–H*), form gridding frameworks enwrap sands. Meanwhile, the ionized calcium hydroxide ($Ca(OH)_2$) also dissolves Al_2O_3 and SiO_2 in sand, and reacted with the dissolved Al_2O_3 and SiO_2 to produce *C-S-H* and *C-A-H* [19]:

$$3Ca^{2+} + 2Si^{4+} + 14OH^- \rightarrow 3CaO.2SiO_2.3H_2O + 4H_2O \quad (5)$$

$$3Ca^{2+} + 4Al^{3+} + 20OH^- + 3H_2O \rightarrow 3CaO.Al_2O_3.Ca(OH)_2.12H_2O \quad (6)$$

As reported previously [19], the strength of the cementitious material increases as the content of *C-S-H* and *C-A-H* increases. A higher content of cement means more C-S-H and C-A-H form in the cementations material, which also indicates the increased compactness of the mortar. Thus, the compressive strength of the sample increases with the cement content.

The compressive strength also increases with increasing curing time (Figure 2). The compressive strength obviously increases with a short curing time (14 d). As the curing time is prolonged from 14 to 28 d, there was no obvious change in compressive strength. Alternatively, as the cement content increased, the increasing rate of compressive strength also decreases with curing time. The high compressive strength in the early stages may relate to slag addition. Wang and Dong [20] also found that the slag addition increases the early-stage compressive strength of concrete when the water-binder ratio exceeded 0.44. The authors attributed this to the chemical reaction between slag and the calcium hydroxide from cement hydration, where the produced C-S-H fills the pore volume and enhances the adhesive strength of the aggregate and binder. As a result, the compactness and strength of the cementitious material increase significantly in the initial stage. As the curing time is extended, less calcium hydroxide is generated from the hydration reaction and less C-S-H is formed at the interface. This means that the compressive strength does not obviously increase in the subsequent period.

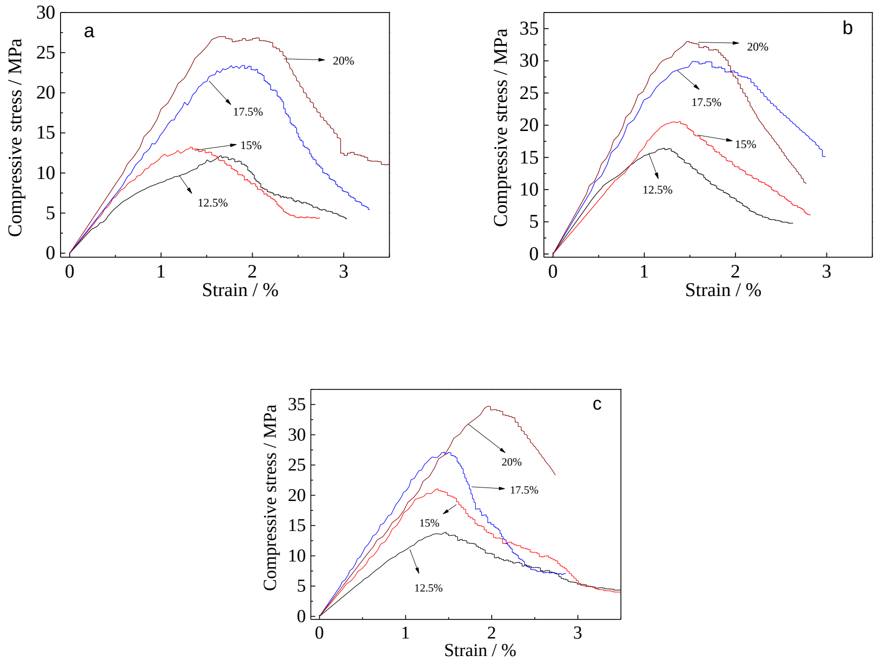


Figure 1. Stress-strain curves of mortars prepared with various cement contents at different curing times of (a) 7, (b) 14 and (c) 28 d.

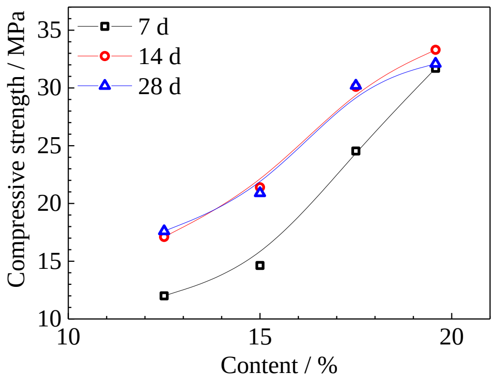


Figure 2. Compressive strength of mortars prepared with different cement contents.

3.2 EIS results

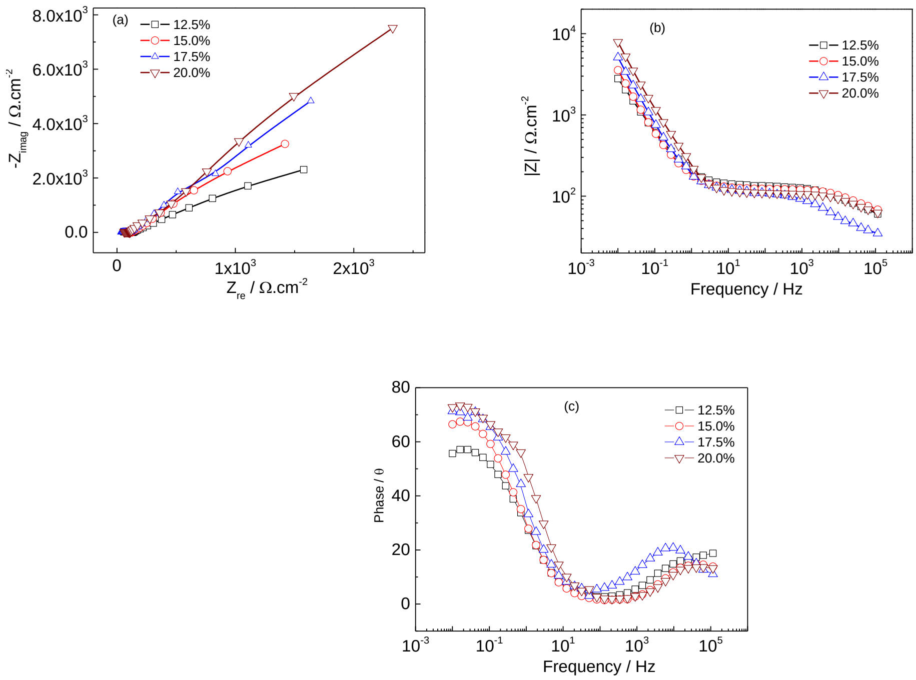


Figure 3. EIS results of mortars at 7 d: (a) Nyquist plots and (b,c) Bode plots.

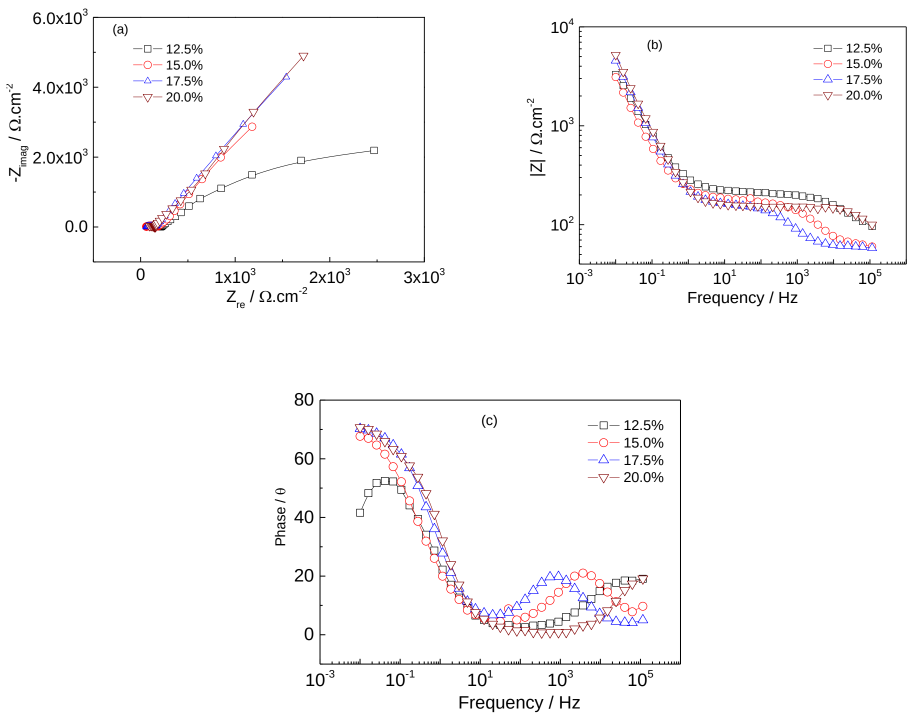


Figure 4. EIS results of mortars at 14 d: (a) Nyquist plots and (b,c) Bode plots.

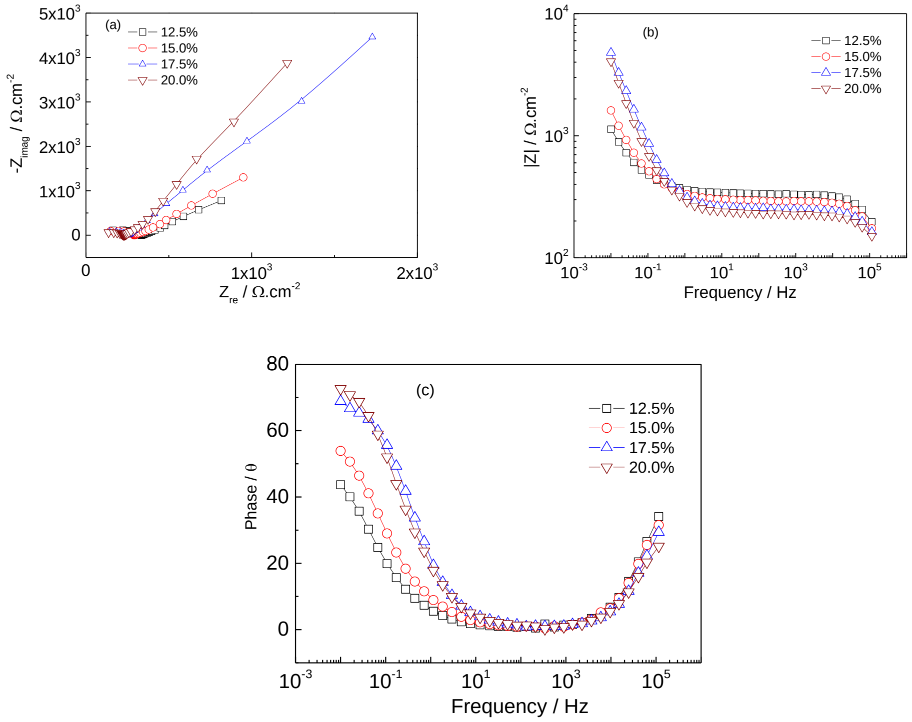


Figure 5. EIS results of mortars at 28 d: (a) Nyquist plots and (b,c) Bode plots.

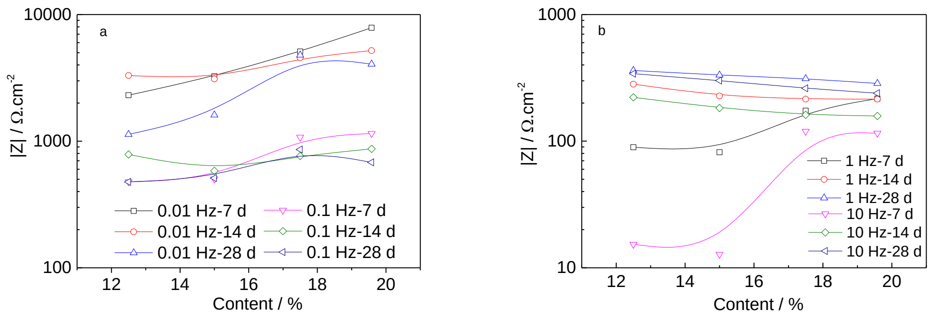


Figure 6. Impedance values of mortars at different frequencies.

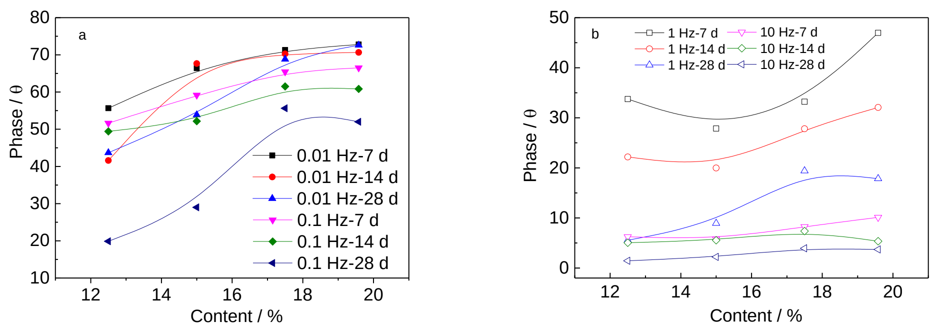


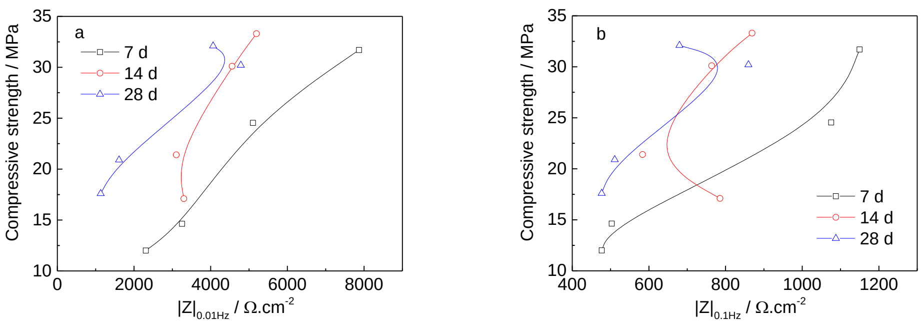
Figure 7. Phase angle of EIS for mortars at different frequencies.

After being immersed in solution for 7, 14 and 28 d, the EIS measurements were carried out for the mortars and the results are presented in Figure 3–5, respectively. As the results show, there are two capacitive arc loops in the Nyquist plots of the mortars. This situation is consistent with the earlier report [7], which attributes the capacitive arc loops to the concrete layer and the concrete/rebar interface, respectively. Alternatively, from the Bode plots shown in Figures 3–5, it is easy to notice that the values of the impedance and phase angle at low frequency increase with the cement content, which suggests that the impedance value and phase angle at low frequency may be used to assess the compactness of cementitious materials.

To further check the impedance values and phase angles at low frequency, the two parameters at 0.01, 0.1, 1 and 10 Hz are analyzed and the results are presented in Figures 6 and 7. The impedance values of mortars at 0.01 and 0.1 Hz increased with the cement content, while that of samples at 1 and 10 Hz decreased with the cement content (Figure 6). However, the phase angle of the mortars always increased with cement content. The value of the phase angle at 0.01 and 0.1 Hz significantly increased and that at 1 and 10 Hz slightly increased with the cement content.

3.3 Relationships between EIS results and compactness

As the compressive strength is closely related to the compactness of cementitious materials [18, 19], the influence of impedance and phase angle on the compressive strength were used to study its effect on compactness. A positive correlation between the compressive strength and the impedance value is observed at 0.01 and 0.1 Hz (Figure 8 and 9). However, a negative correlation between the two parameters is presented at 1 and 10 Hz. In comparison, the phase angle and the compressive strength always present a positive correlation in Figure 9. Moreover, most compressive strength almost linearly increased with the phase angle. This situation suggests that the compactness of the cementitious materials is closely related to the phase angle in the EIS measurements. Consequently, the phase angle may be used as an indicator of the compactness of cementitious materials. Moreover, compared with the methods using an equivalent circuit to assess the compactness of concrete, the phase angle is quite easy and convenient.



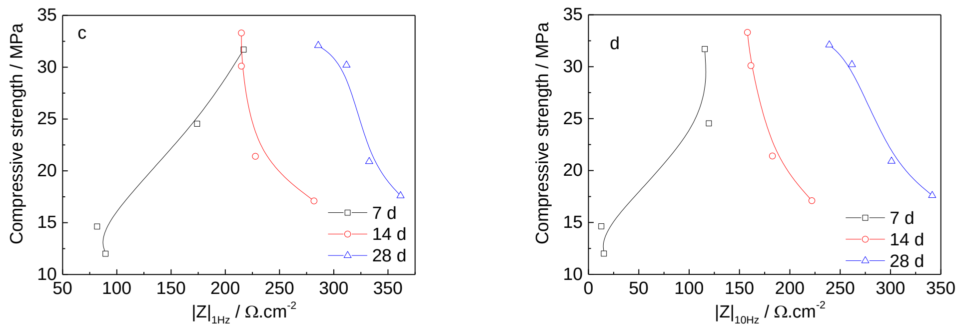


Figure 8. Relationships between compressive strength and impedance for mortars.

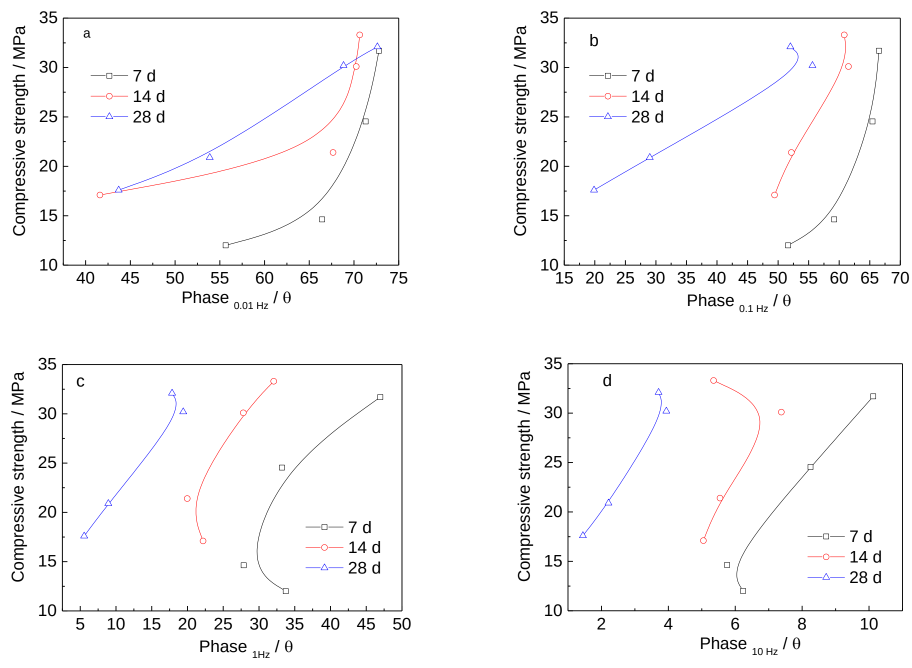


Figure 9. Relationships between compressive strength and phase angle for mortars.

4. CONCLUSIONS

Mortars with different compressive strengths were prepared by 12.5%, 15%, 17.5% and 20% cement, respectively. The compressive strength and electrochemical impedance spectroscopy testing were separately performed on the mortars at 7, 14 and 28 d. The following conclusions can be drawn:

(1) The compressive strength increased with the content of cement, for the compactness of the cementitious materials is enhanced by the cement.

(2) The values of impedance and phase angle in EIS results are closely related to the compressive strength of the samples. The compressive strength of the mortars increased with the impedance value at the frequency of 0.01 and 0.1 Hz, while that decreased with impedance at the frequency of 1 and 10 Hz. Alternatively, the compressive strength always increased with the phase angle when the frequency was lower than 10 Hz in the present study.

(3) Compared with the impedance values, the phase angle is a more effective and convenient indicator to assess the compressive strength of cementitious materials.

ACKNOWLEDGEMENTS
The present work is supported by the Natural Science Foundation of Jiangsu Province (BK20151498).

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