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Communication

A study of polymer-modified mortars by the AC impedance technique

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Abstract

Cement mortar can be regarded as a composite consisting of the cement paste, fine aggregate, and the interfacial transition zone (ITZ). In this paper, the formation and development of the ITZ of polymer-modified mortar (PMM) was studied by alternating current impedance spectroscopy (ACIS). The test results showed that the AC impedance spectra of the PMMs had the following characteristics: (1) the AC impedance spectra of the fresh PMMs were almost parallel to the imaginary axis; (2) The AC impedance spectra of the hardened PMMs showed a high-frequency part not connected to the intermediate frequency part. This characteristic was maintained over a rather long period, and then obvious changes appeared in the AC impedance spectra. The age at which the impedance spectra of the mortars changed appeared to shorten with an increase of the sand volume fractions (SVFs). These characteristics of the AC impedance spectra of the PMMs were related to the close contact, the packing, and the formation of a mechanically rigid film of the polymer particles.

Keywords: Polymer-modified mortar; Interfacial transition zone; Alternating current impedance spectrum

1. Introduction

It is well known that the performance of cement mortar and concrete can be improved by polymers [1–3]. The mechanisms of the improvements have been studied by many researchers [4–7]. For the sake of simplicity, polymer-modified mortar (PMM) in which coarse aggregate was dispensed with was studied with a view to elucidate the alternation of the interfacial transition zone (ITZ) between the cement paste and the sand. There have been many studies conducted using alternating current (AC) impedance of cement pastes and mortars [8–10]. AC impedance spectroscopy (ACIS) is now a powerful tool generally accepted in the study of cement paste and concrete, and is the technique adopted for the present work. This paper presents some data on the complex impedance of polymer-modified paste and mortars measured at various ages during the hardening process. The film process by which polymer particles form films and the formation and development of the ITZ of PMM could be studied this way.

2. Experimental

The mortar specimens were prepared by mixing Portland cement (P II 525R), water, styrene–acrylic ester (SAE), and monosized sand with a water/cement ratio of 0.45 and a polymer/cement ratio of 0.15. The particle sizes of monosized sands were: 180–315 μm, 315–450 μm, 450–560 μm, and 560–710 μm. The sand volume fractions (SVFs) of the different mortars were 0.00, 0.05, 0.13, 0.20, 0.28, 0.37, 0.44, 0.51, and 0.56. For the AC impedance measurements, two electrodes consisting of stainless steel sheets 4×4 cm^2 were used. The electrodes were fixed in a plastic frame to maintain separation of 2 cm. The frame with the electrodes was then placed in a plastic cup, and mortar was cast into the cup. After the first measurement, the cup containing the specimen was sealed with plastic film. After 1 day, the top of the mortar was sealed with latex paint. Specimens were stored in a laboratory atmosphere (20 ± 2 °C, 90% RH).

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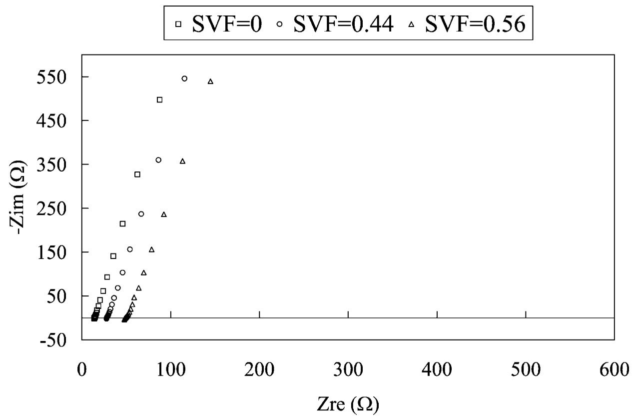

Fig. 1. AC impedance spectra of fresh PMMs with different SVFs (sand size 180–315 μm).

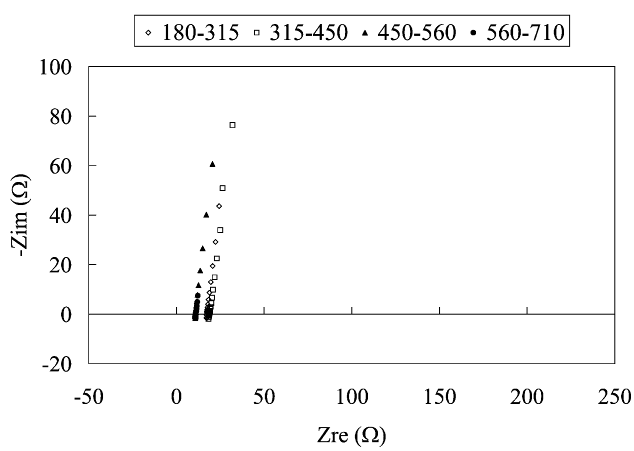

Fig. 2. AC impedance spectra of fresh mortars with different sand particle sizes (μm) (SVF = 0.05).

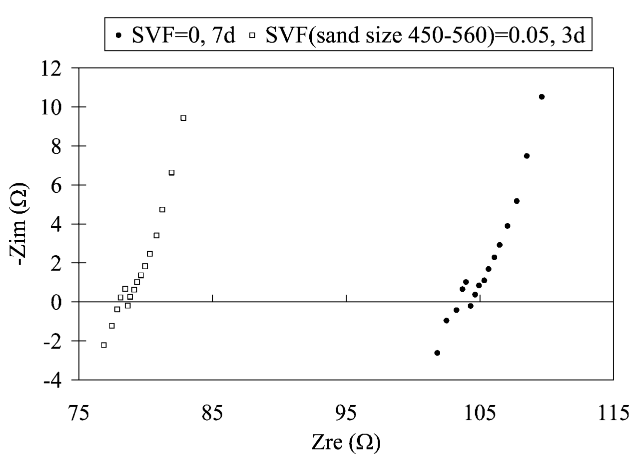

Fig. 3. Typical AC impedance spectra of PMM after 3 days of curing.

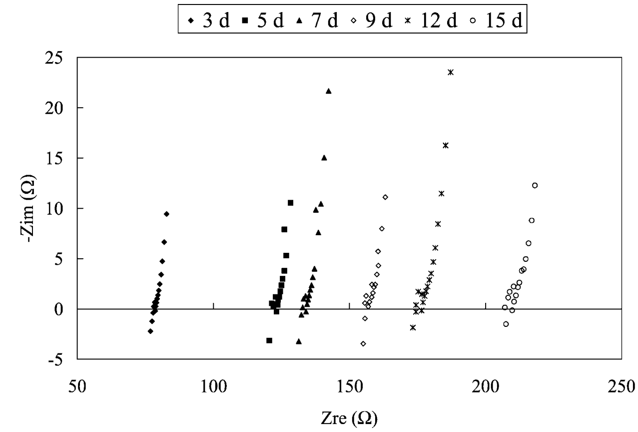

Fig. 4. AC impedance spectra of specimens with sand size of 450–560 μm and SVF = 0.05 at ages of 3, 5, 7, 9, 12, 15 days.

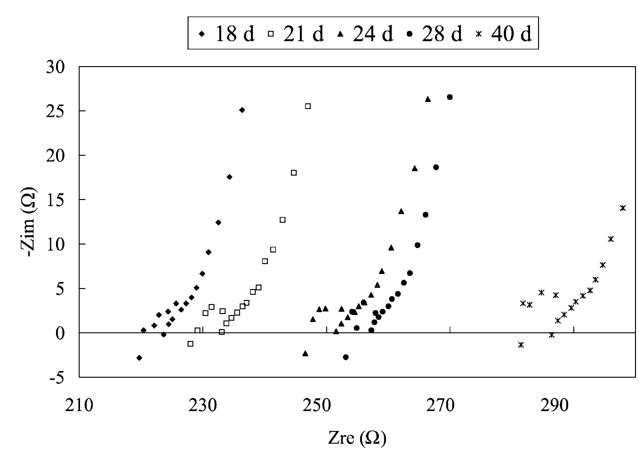

Fig. 5. AC impedance spectra of PMM at ages of 18–40 days (SVF = 0.05, sand size 450–560 μm).

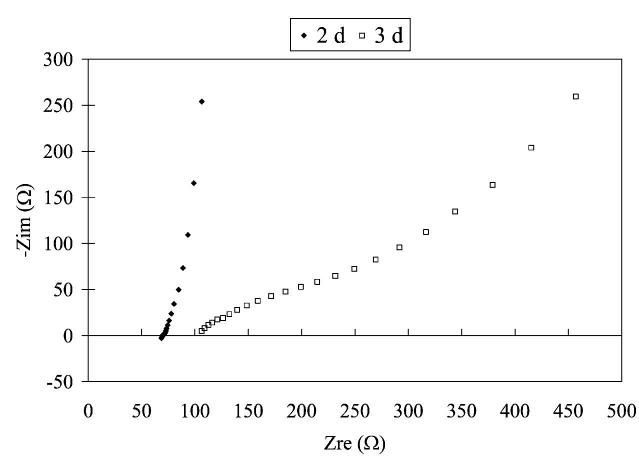

Fig. 6. AC impedance spectra of cement paste with w/c = 0.4.

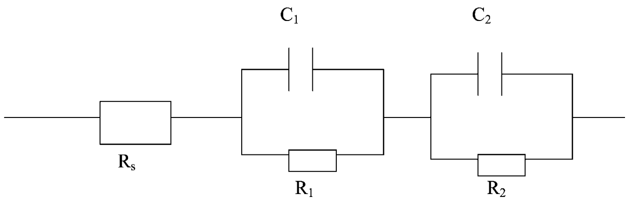

Fig. 7. Equivalent circuit of Fig. 3.

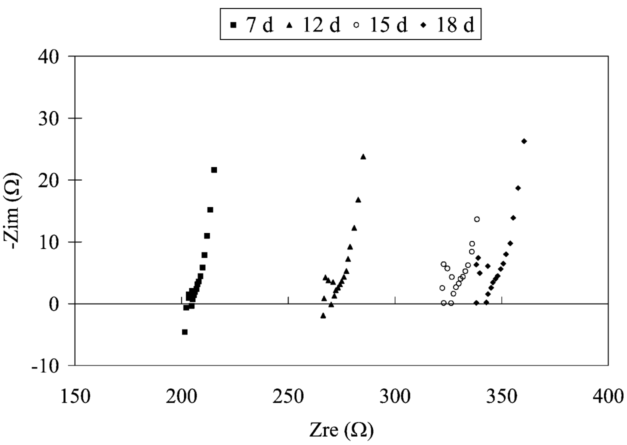

Fig. 8. AC impedance spectra of specimens with SVF = 0.2 and sand size of 450–560 μm at ages of 7–18 days.

The AC impedance measurements were taken with Potentiostat Model 273A and Lock-in Amplifier Model 5210 manufactured by EG&G PARC. A sinusoidal voltage at an amplitude of 5 mV was used. The frequency range was 100 kHz–1 Hz.

3. Results and discussion

3.1. AC impedance spectra of the fresh PMMs

The AC impedance spectra of the fresh PMMs are shown in Figs. 1 and 2. Fig. 1 displays the AC impedance spectra of fresh PMMs with different SVFs, while Fig. 2 presents the AC impedance spectra of the fresh PMMs with different sand particle sizes. It is obvious from Figs. 1 and 2 that the impedance response of the fresh PMMs is a line almost parallel to the imaginary axis. For the fresh PMMs with different sand particle sizes, the impedance spectra are approximately overlapped. In this early stage, only a small amount of cement hydration C-S-H gel was formed, so the process of charge transfer did not occur [11].

3.2. AC impedance spectra of hardened PMMs

Fig. 3 shows typical AC impedance spectra of PMM after 3 days of curing. At that time, the AC impedance spectra are characterized by a high-frequency arc not connected to the intermediate frequency curve. This is maintained over a rather long period. In Figs. 4 and 5, the AC impedance spectra of the specimen with sand size of 450–560 μm and SVF = 0.05 at ages from 3 to 40 days are presented. This behavior is characteristic of PMMs. As a comparison, Fig. 6 displays the AC impedance spectra of cement paste with a water/cement ratio of 0.4.

The AC response of the hardened PMMs could be described using the equivalent circuit shown in Fig. 7. The parallel combination of resistor R_1 and capacitor C_1 should account for the behavior of the polymer concentrated in the ITZ.

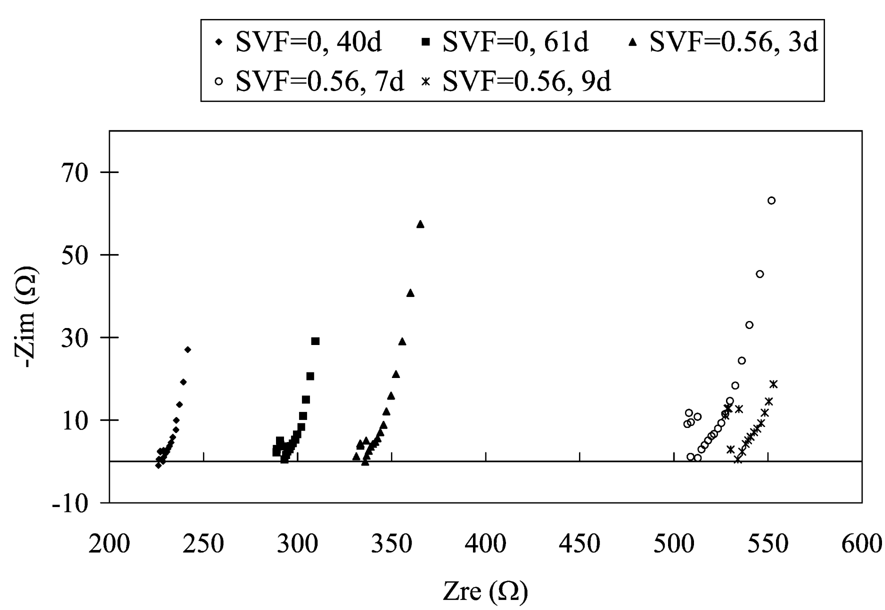

Fig. 9. AC impedance spectra of specimens with different SVFs at different ages (sand size 450–560 μm).

It is noticeable from Fig. 5 that the form of the high-frequency portion varies somewhat. However, a great change appears at a certain age depending on the SVFs of the PMMs. This change can be noticed as the second change. Fig. 8 shows the spectra of the specimens with a sand size of 450–560 μm and SVF = 0.05, and Fig. 9 the spectra of specimens with SVF = 0 and SVF = 0.56. For the specimen with SVF = 0, the second change does not appear at 61 days, while for the specimen with SVF of 0.56 the second change appears by 7 days (Fig. 9). In the specimen with the medium SVF of 0.2, the second change appears at 15 days (Fig. 8).

The changes of the AC impedance spectra of the PMMs may be related to the film formation process of polymer latex. The film formation process of latex can be divided into three stages. In Stage I, the polymer particles come together due to water evaporation or reduction. In Stage II, the polymer particles deform and form a close-packed particle structure. In Stage III, the packed particles interact further to form a mechanically rigid film when the temperature is high enough or when the time is long enough [12]. The structures of the polymer formed during Stage II and Stage III have distinct differences. They must then exhibit different AC responses. Thus, the first change of the AC impedance spectra of the PMMs may be associated with Stage II, and the second change to Stage III. In other words, through the AC impedance measurements, we could follow the film formation process of latex in cement mortar and determine the expected curing time for film formation of latex in the cement mortar.

4. Conclusion

The AC impedance spectra of hardened PMMs were characterized by a high-frequency arc not connected to the intermediate frequency curve. This characteristic was maintained for a rather long period, and then an obvious change appeared in the AC impedance spectra. The age at which the changes of the impedance spectra of the mortars appeared decreased with an increase of the SVFs. The first change may be related to the formation of a close-packed structure of the polymer particles, and the second change to the formation of a mechanically rigid film of the polymer particles. Through the AC impedance measurements, we could follow the film formation process of latex in the cement mortar. For the SAE latex used in the current study, the film formation process occurred after water was consumed by cement hydration or absorbed by sand, as described by Ohama [1].

References

[1] Y. Ohama, Handbook of Polymer-Modified Concrete and Mortars, Properties and Process Technology, Noyes Publications, New York, 1995.

[2] S. Zhong, G. Gu, Z. Chen, Research and development of polymers in concrete in China, Proceedings of the Third Asia Symposium on Polymers in Concrete, Nov. 20–23, Shanghai, China, Tongji University Press, Shanghai, China, 2000, pp. 3–13.

[3] G.W. De Puy, Polymer-modified concrete—properties and applications, International ICPIC Workshop on Polymers in Concrete for Central Europe, Bled, Slovenia (1996) 63–67.

[4] A. Beeldens, J. Momteny, E. Vincke, N. De Belie, Influence of polymer type on the structure of polymer modified cement mortar, Proceedings of the 21st International Conference on Cement Microscopy (CD-ROM), Las Vegas, USA, April 25–29, International Cement Microscopy Association, Ducanville, Texas, USA, 1999.

[5] M. Puterman, W. Malorny, Some doubts and ideas on the microstructure formation of PCC, Proceedings of IXth International Congress on Polymers in Concrete, Bologna, 1998, pp. 166–178.

[6] J. Schulz, O. Killerman, Long-term performance of redispersible powders in mortars, Cem. Concr. Res. 31 (3) (2001) 357–362.

[7] A. Beeldens, J. Monteny, E. Vincke, N. De Belie, D. Van Gemert, L. Taerwe, W. Verstraete, Resistance to biogenic sulphuric acid corrosion of polymer-modified mortars, Cem. Concr. Compos. 23 (1) (2001) 47–56.

[8] W.J. McCarter, S. Gravin, N. Bouzid, Impedance measurements on cement paste, J. Mater. Sci. Lett. 7 (1988) 1056–1057.

[9] W.J. McCarter, R. Brousseau, The A.C. response of hardened cement paste, Cem. Concr. Res. 20 (1990) 891–900.

[10] K. Brantervik, G.A. Niklasson, Circuit models for cement based materials obtained from impedance spectroscopy, Cem. Concr. Res. 21 (1991) 496–508.

[11] Y. Zhang, M. Shi, Study of the A.C. impedance spectrum of cement-based materials, J. Build. Mater. 3 (2) (2000) 109–112 (in Chinese).

[12] J. Feng, M.A. Winnik, R.R. Shivers, B. Clubb, Polymer blend latex films: morphology and transparency, Macromolecules 28 (1995) 7671–7682.