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Combined time domain reflectometry and AC-impedance spectroscopy of fiber-reinforced fresh-cement composites

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Abstract

Time domain reflectometry and conventional AC-impedance spectroscopy were combined to investigate the impedance response of fiber-reinforced fresh-cement composites over a broad frequency range (0.1 Hz to 1 GHz). With proper attention to inductive effects at high frequency, conventional AC-IS can be employed to evaluate important fiber dispersion issues (fiber orientation, segregation, and clumping) in fresh-cement matrix composites.

Keywords: Dispersion; Fresh concrete; Electrical properties; Composite; Fiber reinforcement

1. Introduction

Fiber dispersion is a crucial factor determining the properties of fiber-reinforced composites (FRCs) [1–3]. Fiber-reinforced cement-based composites are currently employed in semi-structural applications, but their use could be extended to more demanding structural applications if their mechanical performance (i.e., ductility, toughness, and strength) were further improved. We have recently demonstrated the use of AC-impedance spectroscopy (AC-IS) to characterize various fiber dispersion issues in FRCs with discontinuous conducting fibers [4–6]. AC-IS provides a non-destructive method to evaluate the orientation, coarse segregation, and local aggregation of fibers.

Previous studies on fiber dispersion have involved hardened cement paste composites. Analysis and characterization of fresh cement-based composites, prior to hardening, would provide the earliest indicators for eventual composite microstructure, including fiber dispersion evaluation [4]. Monitoring fresh cement during processing (e.g., during mixing and extrusion) would allow for adjustment of parameters to prevent or remedy undesirable effects arising from the unintentional alignment of fibers or fiber clumping. However, owing to the high electrical conductivity of fresh cement paste and instrumental/experimental limitations, the interpretation of AC-IS data for fresh cement-based composites is difficult.

Extensive work has been done exploring the use of electrical measurements, in particular AC-impedance spectroscopy (AC-IS), to examine fresh or early-age plain cement paste or concrete (i.e., without fiber additions) in an effort to predict strength, which is linked to the service life of concrete structures [7]. However, immediately upon mixing and prior to set, AC impedance spectra tend only to show the electrode response, with little or no bulk cement response, since it is overwhelmed by parasitic inductive contributions from leads and cabling [8–12]. Fortunately, another method, time domain reflectometry (TDR), can be used to extend the IS frequency range as high as 1 GHz, and without being as susceptible to parasitic inductive contributions. Hager and Domszy [13] pioneered the use of TDR to investigate the hydration of plain ordinary Portland cement (OPC) prior to hardening. This work combines TDR and AC-IS to examine fresh cement-based composites reinforced with steel fibers.

2. Experimental procedures

Fresh cement paste composite samples were produced using type I ordinary Portland cement (OPC) and steel fibers (0.05 vol %, 2 mm long, 30 μm diameter). Fibers were dry-

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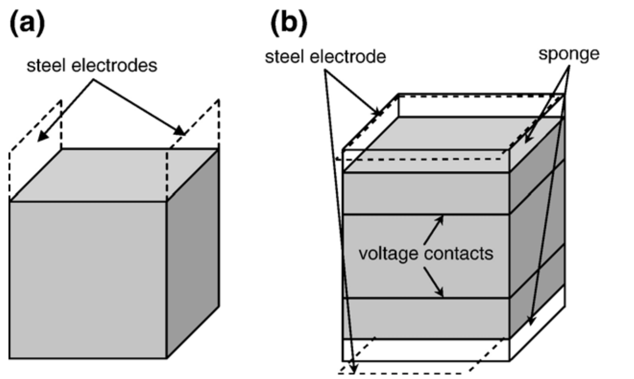

Fig. 1. Experimental setup for AC-impedance spectroscopy (AC-IS) measurements of (a) fresh cement paste samples at early times using imbedded steel electrodes and (b) hardened cement paste samples using "wet" sponge electroding.

mixed with the cement powder by hand for 2 min. Water was then added to achieve a 0.4 w/c ratio, followed by hand-mixing for approximately 2 min. The mixture was then blended at low speed in a Hobart planetary mixer for 2 min, and then at high speed for another 2 min. By magnetic separation and optical microscopy, a sampling of fibers from a similarly processed fresh paste showed no noticeable alteration in fiber geometry (i.e., bending or length changes) due to processing [14]. Plain OPC specimens (without fibers) were mixed in a similar manner. Time zero was considered to be when the cement powder contacted the water. Both AC-impedance spectroscopy (AC-IS) and time domain reflectometry (TDR) were used to make initial measurements at 20 min, and then periodically up to 4 h. In addition, AC-IS measurements were made on the same samples after hardening for 1 day and 7 days.

2.1. AC-impedance spectroscopy (AC-IS)

For the AC-IS experiments, samples were cast into cubes using polycarbonate molds that were 86 mm on a side. Large 0.5 mm thick stainless steel plate electrodes were imbedded into the composite during casting to serve as leads for the two-point AC-IS measurements prior to hardening. Fig. 1a shows the imbedded electrode setup. After measurements were made on the fresh cement samples, they were cured in a moist environment for 24 h. Samples hardened for 1 day were demolded and contacted using a "wet" electroding technique involving thick stainless steel plate electrodes lightly pressed against the sample surfaces with sponges, as shown in Fig. 1b. The sponges were soaked in an ionically conducting solution that was in intimate contact with each end of the sample. The ionic solution was a synthetic pore solution consisting of 0.33 M potassium hydroxide and 0.13 M sodium hydroxide in an attempt to replicate the major species (and electrical conductivity) of pore solution. It was based on atomic absorption spectrometry data from pore fluid extracted from the composite samples. Measurements were also made on the 7-day old samples using the same technique.

AC-IS measurements were made using a Solartron 1260 impedance/gain-phase analyzer with Z-60 personal computer software for data acquisition (Schlumberger, Houston, TX). Samples were subjected to an excitation voltage of 1 V and scanned from 11 MHz to 0.1 Hz at 20 steps per frequency decade.

Four-point DC measurements were performed on 7-day old hardened samples to obviate external electrode contributions in the AC-IS measurements thereby confirming low-frequency cusp values. Tightly wrapped 0.25 mm diameter steel wire loops at 1/4 and 3/4 positions along the sample served as voltage contacts, while current was applied to the outer electrodes (steel plate electrodes/sponges) in 1 mA increments from 10 mA to −10 mA, as seen in Fig. 1b. DC measurements were made using a programmable current source and digital multimeter (Keithley, Models 220 and 2000, Cleveland, OH) using LabVIEW personal computer software for data acquisition. DC-derived resistance values were geometry-corrected (from $L/2$ to L, where L = sample length) for comparison with AC-IS data on Nyquist plots.

2.2. Time domain reflectometry (TDR)

TDR measurements were made using a cylindrical sample geometry that was 31 mm in length and 22 mm in diameter, as seen in Fig. 2. TDR, similar to AC-IS measurements, involves two leads, but in a radial geometry (i.e., with an inner and outer electrode) as opposed to two opposing planar electrodes for AC-IS as seen in Fig. 1a and b. Electrical contact for the TDR measurements involved stripping a coaxial cable (semi-rigid UT 141, 3.5 mm) to expose an 8 mm length of the inner conductor, which was then inserted into the fresh paste. The wall of the sample cell served as the outer conductor by contacting the outer part of the coaxial cable through a Teflon disk covered in aluminum foil. TDR traces were taken initially at 15 min after mixing and then periodically for up to 1 h. Data from the TDR were interpreted using the empty cell capacitance of the sample cell, which was calibrated with standard liquids with known dielectric properties (acetone, methanol, and deionized water).

A broadband technique, TDR enables characterization to higher frequencies (from 10^3 to 10^9 Hz) than AC-IS, which ranges from 10^{-3} to 10^7 Hz. Fig. 3 shows a schematic of how TDR operates. A coaxial transmission line terminates in the

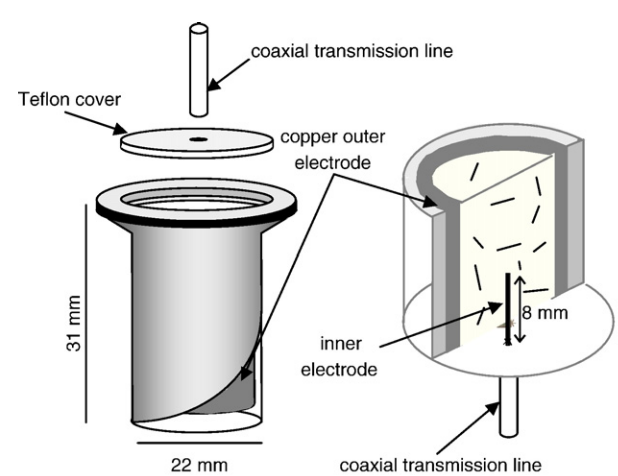

Fig. 2. Large cylindrical sample cell used for time domain reflectometry (TDR) measurements.

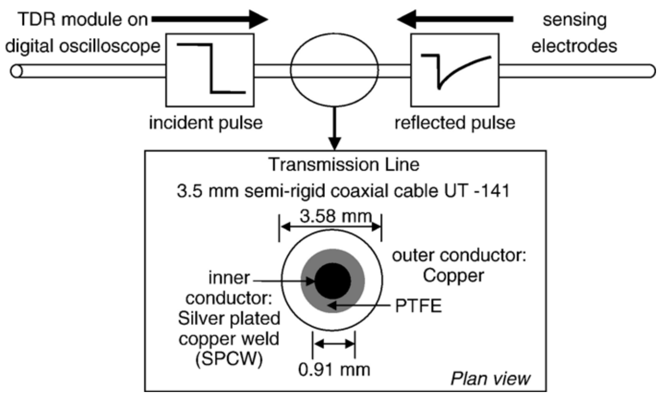

Fig. 3. Schematic demonstrating how time domain reflectometry (TDR) measures the high-frequency dielectric behavior of materials.

cylindrical cell, which contains the sample. An HP 54120 digitizing oscilloscope with a 54121A TDR sampling head sends an incident voltage pulse with a very short rise time (20 ps) along the transmission line and measures the reflected voltage pulse, which includes quantitative information about the complex dielectric properties of the sample. Consecutive segments of the TDR reflected transient are analyzed using PC-automated data acquisition and a variable-time-scale sampling method developed by N.E. Hager [15]. The reflected transient is then transformed into the frequency domain using a numerical Laplace transform. Details of the expressions used to interpret TDR are described elsewhere in the literature [13,15].

3. Results and discussion

3.1. Using AC-IS to characterize composites

AC-IS entails using a frequency response analyzer and surface electrodes to apply low-amplitude AC excitation over a range of frequencies and to measure the current response, which includes the gain and phase angle. Each frequency produces a single datum that can be plotted on a Nyquist plot (negative imaginary impedance vs. real impedance) where frequency increases right to left. Fig. 4a shows data for a hardened cement sample, with and without steel fibers, at 7 days. Frequency markers are shown as darkened points with corresponding numbers representing Log of frequency in Hz.

The correspondence of the single cusp in the plain cement sample with the low-frequency (LF) cusp of the composite is due to an oxide coating on the steel fibers, which renders them insulating at low frequencies. The LF-cusps of the plain cement and composite also match the measured DC-resistance values (shown as discrete points on the x-axis/real impedance axis). Data to the left of these cusps reflect the bulk response(s); data to the right reflect the electrode response (only a portion of which is shown). At higher frequencies, displacement currents short out the oxide coating, producing a second cusp in the composite, labeled R_{cusp}, with a smaller resistance (real impedance) value indicating the influence of the conducting fibers. The demonstrated "dual-cusp" behavior allows AC-IS measurements to determine both the resistance of the plain cement, which is measured at low frequencies due to the oxide coating, as well as the lower resistance of the composite with conductive fibers, which is measured at higher frequencies. Therefore, the low-frequency cusp (LF-cusp) value provides the resistance of the matrix, R_{DC}, and the high-frequency cusp (HF-cusp) value provides the resistance of the composite, R_{cusp}, with the fibers "active" (conducting). The ratio between the two resistance values can be interpreted using composite theory and an "intrinsic conductivity" approach in order to characterize fiber dispersion [5]. For example, with larger fiber loading and/or with fiber alignment, the value of R_{cusp} dramatically decreases. In contrast, fiber clumping reduces the influence of the fibers such that R_{cusp} increases. Extensive discussion of cement composite AC-IS behavior and its interpretation in terms of fiber dispersion (alignment, segregation, clumping) are provided elsewhere [4–6].

3.2. Electrical properties of fresh-cement paste

Christensen et al. [16] provides a good review for the use of AC-IS in hydration studies. Immediately after cement powder is contacted by water, a highly conductive (low-resistivity) ionic slurry forms that continually increases in resistance during curing and hardening due to the decreasing amount of

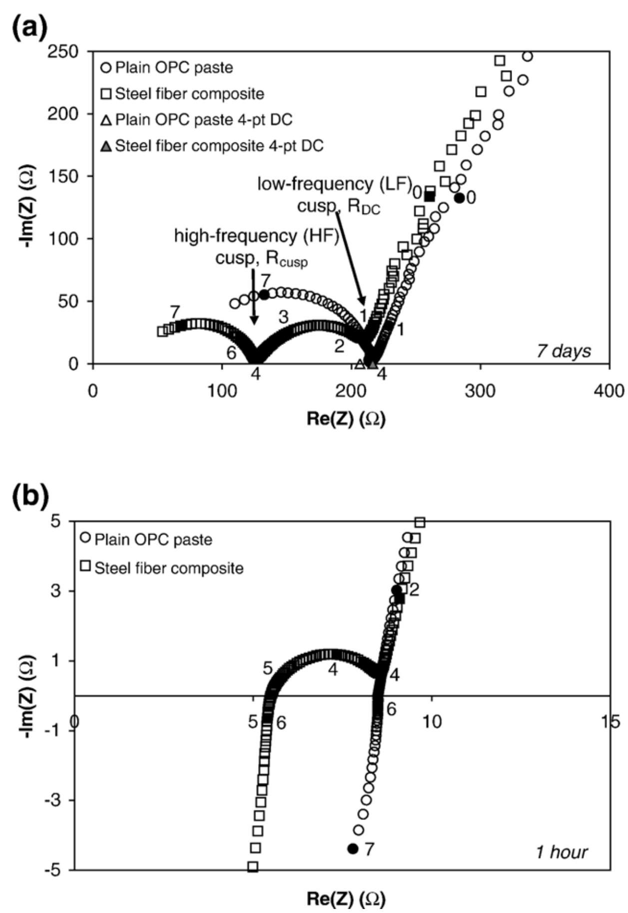

Fig. 4. Nyquist plot of plain ordinary Portland cement (OPC) paste, with and without 0.5 vol.% steel microfibers (~2 mm long and ~30 μm in diameter) at (a) 7 days, and (b) 1 h. Numbers corresponding to darkened points and cusps are Log frequency (Hz) markers.

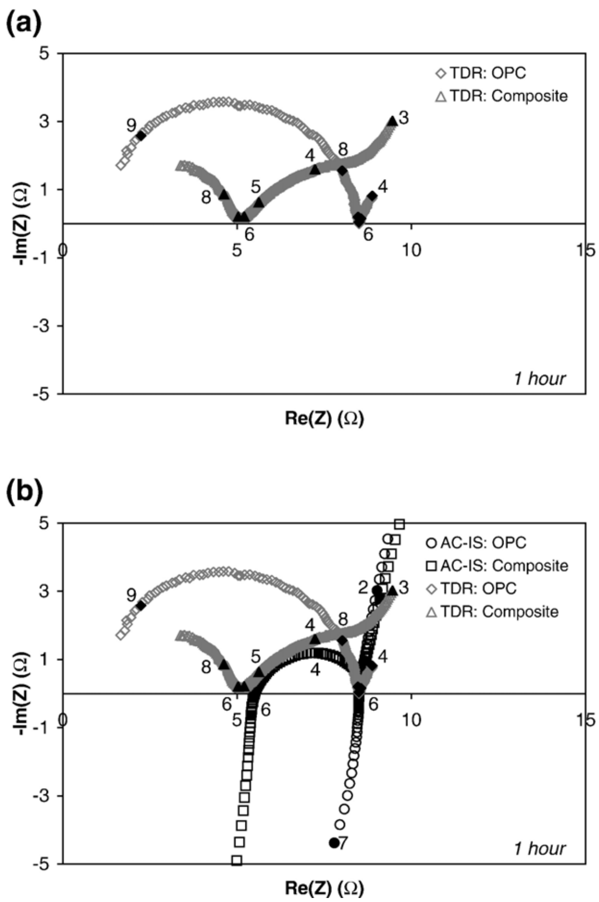

Fig. 5. Nyquist plot of (a) time domain reflectometry (TDR) data for plain ordinary Portland cement (OPC) paste, with and without 0.5 vol.% steel microfibers (~2 mm long and ~30 μm in diameter) and (b) TDR data plotted alongside AC-impedance spectroscopy (AC-IS) results. Numbers corresponding to darkened points and cusps are Log frequency (Hz) markers.

evaporable water and the decreasing connectivity, or increasing tortuosity, of the pore network. The initial low resistivity of fresh cement paste results from the high concentration of mobile ions in the pore fluid combined with high connectivity of the capillary porosity. Low measured resistances can result in the bulk AC-IS response being swamped out by inductive reactances from electrodes and cabling.

The time constant of the fresh cement is quite small ($RC \sim 10^{-9}$) such that the features of the bulk material (fresh cement paste) lie near the upper frequency limit of conventional impedance analyzers. At high frequencies, the cables, leads, sample holder, etc., can all contribute stray immittances, or additional resistance and inductance, to the measurements of low resistance, high capacitance samples such as fresh cement paste [17,18].

Whereas both cusps are clearly evident in Fig. 4a, as discussed above, the data taken at 1 h, as shown in Fig 4b, show no cusp in the plain cement data (open circles) and only a single cusp for the composite data (open squares). At high frequencies, the plain cement data begin to fall below the real impedance axis to positive values of imaginary impedance, with no evidence of a bulk arc. For the composite data (open squares), a single cusp is evident at lower frequencies, as seen in Fig. 4b, with a discernable value for R_{DC}. The high-frequency behavior of the composite (Fig. 4b), similar to the plain cement paste, has data falling below the real impedance axis, with no evidence of a high-frequency bulk arc or HF-cusp (R_{cusp}). Therefore, for fresh cement-based materials, at early times, the values of R_{DC} and R_{cusp} are difficult to discern from the Nyquist plot, and AC-IS based fiber characterization methods (i.e., for fiber dispersion) are in question [5].

4. TDR and AC-IS

Fig. 5a shows the Nyquist plot of data taken with TDR at 1 h for the plain cement and composite. In contrast to the AC-IS data, the LF-cusp value (R_{DC}) of the plain cement is clearly seen in the TDR data (Fig. 5a), with almost the entire bulk arc visible at frequencies into the GHz range. The high-frequency capabilities of TDR allow measurements of the highly conductive fresh cement without the complications from system inductive contributions (i.e., from cables, leads, etc.). Similarly, for the composite, TDR measurements allow the HF-cusp value (R_{cusp}) to be determined, and again, most of the high-frequency bulk arc is visible (Fig. 5a).

Fig. 5b plots the 1 h TDR data along with the AC-IS data of fresh cement paste with and without fibers for comparison. Good

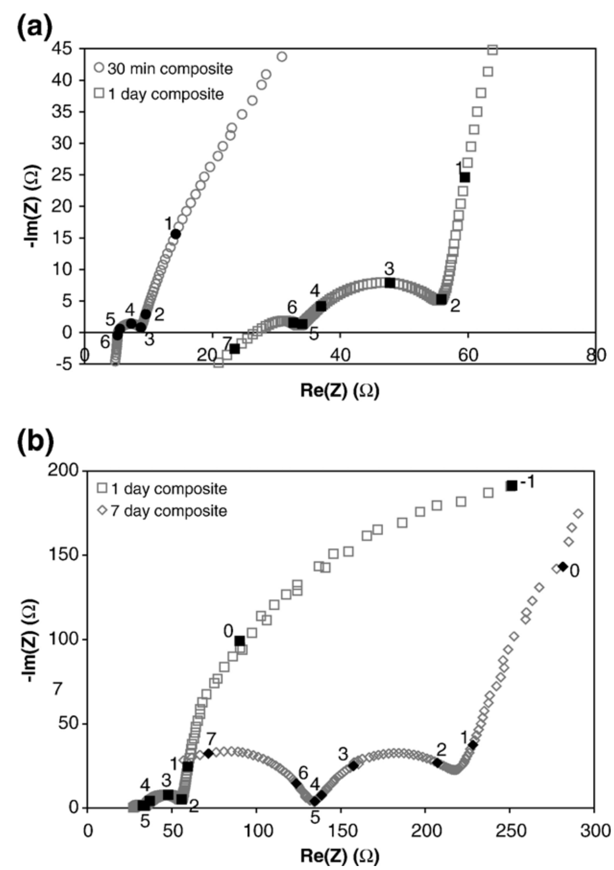

Fig. 6. Nyquist plot of plain ordinary Portland cement (OPC) paste composite with 0.5 vol.% steel microfibers (~2 mm long and ~30 μm in diameter) tested at (a) 30 min and 1 day, and (b) 1 day and 7 days. Numbers corresponding to darkened points and cusps are Log frequency (Hz) markers.

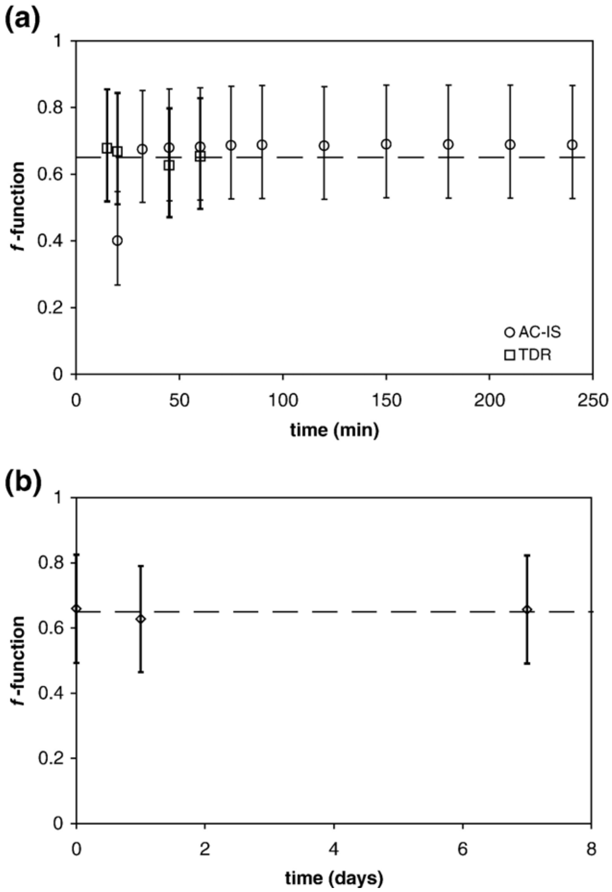

Fig. 7. The *f*-function (see text and Refs. [6,19]) calculated from Nyquist data at (a) early times using TDR and AC-IS and (b) 0, 1, and 7 days using AC-IS. The dashed line shows the averaged value of *f*-function for all data taken (early, 1 day, and 7 days) and has a value of 0.65.

agreement is found between the two methods. In Fig. 5b, TDR demonstrates that AC-IS is able to determine the value of the LF-cusp (R_{DC}) in the plain cement sample, and the values of both the LF-cusp (R_{DC}) and HF-cusp (R_{cusp}) in the composite sample, even though the bulk arcs are not evident. TDR confirms that the point where the data on the Nyquist plot begin to fall below the real impedance axis (positive values of imaginary impedance) can be interpreted as corresponding to the LF-cusp (R_{DC}) in the plain OPC paste and the HF-cusp value (R_{cusp}) in the composite. Although the system inductive contributions distort the high-frequency bulk arc, the cusp value is not significantly altered. However, larger amounts of system inductive contributions in the AC-IS measurements could cause the cusp value to be unreliable and are therefore addressed in Appendix A using equivalent circuit analysis. Nevertheless, the data demonstrate that TDR and AC-IS can be combined to allow characterization of AC-IS response over a much larger frequency range.

5. Analysis of fresh cement paste composites

Fresh cement paste continues to increase in resistance with time as the cement hardens and cures, as demonstrated by the increasing cusp values in the Nyquist plots, where Fig. 6a shows 30-min and 1-day data, and Fig. 6b shows 1-day and 7-day data. Also, the high-frequency limitations of the impedance analyzer become less a factor owing to the increasing resistance of the cement. Whereas both the 30-min and 1-day data have data below the real impedance axis, indicating inductive contributions, the 7-day data do not. This is because the resistance of the composite has increased to a sufficiently high value so that the data are no longer vulnerable to distortion at high frequencies.

The parameter used to characterize fiber dispersion in composites is related to the ratio of the LF-cusp resistance value (R_{DC}) and the HF-cusp resistance value (R_{cusp}), which is referred to as the normalized conductivity. This is the same as the ratio of the composite conductivity (σ) and the matrix conductivity (σ_m) (See Section 3.1). To further isolate the effect of fibers, an *f*-function has been defined as $(1-\sigma/\sigma_m)$ [6]. This function reflects the product of intrinsic conductivity (which can be predicted for a given aspect ratio of fibers) and fiber loading (or volume fraction). It is highly sensitive to factors such as fiber orientation, segregation, and clumping. The AC-IS method for characterization of fiber dispersion using both the normalized conductivity and *f*-function is discussed elsewhere [4–6].

The normalized conductivity, and therefore the *f*-function, should be independent of the absolute value of the measured resistance, i.e., arising from changes in matrix conductivity, assuming that no other change in microstructure occurs upon hardening. Fig. 7a shows the values of the *f*-function calculated at early times (15 min up to 4 h) for both the TDR and AC-IS data. Fig. 7b shows the values of the *f*-function calculated at 0, 1, and 7 days. The 0-day value in Fig. 7b is the average of all AC-IS data taken up to 4 h, which are all very similar. The average of all AC-IS data taken, regardless of time, produces an *f*-function value of 0.65, which is shown as a dashed line in Fig. 7a and b. Good agreement is seen between the calculated values of the *f*-function between the AC-IS and TDR for early times, as well as between early values and values taken after the cement hardens (1 day and 7 days). This suggests that

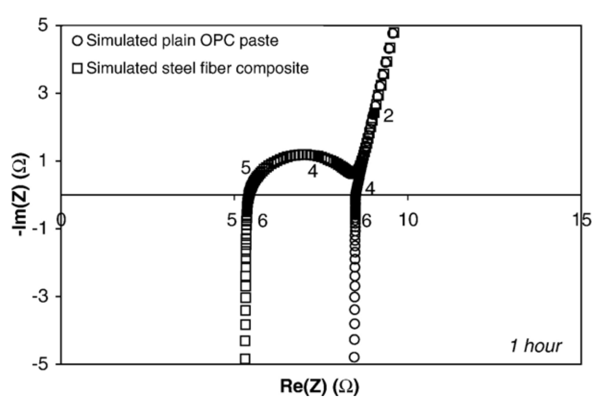

Fig. A.1. Simulated Nyquist plots for plain ordinary Portland cement (OPC) paste, with and without 0.5 vol.% steel microfibers (~2 mm long and ~30 μm in diameter) at 1 h (see Fig. 4b). The following parameters were employed (Boukamp notation, see Refs. [14,19]): $L([R(RQ)(RQ)][(RQ)(RQ)])(RQ)$= 1×10^{-7} H, 0.01 or 10^9 Ω, 14.1 Ω, 1.99×10^{-10} F (0.897), 2.78×10^6 Ω, 4.32×10^{-6} F (0.8), 8.49 Ω, 3.31×10^{-10} F (0.897), 4.98×10^{-2} Ω, 5.64×10^{-8} F (0.897), 2.78×10^2 Ω, 1.52×10^{-3} F (0.87), with *n*-values (see Refs. [14,19]) in parentheses.

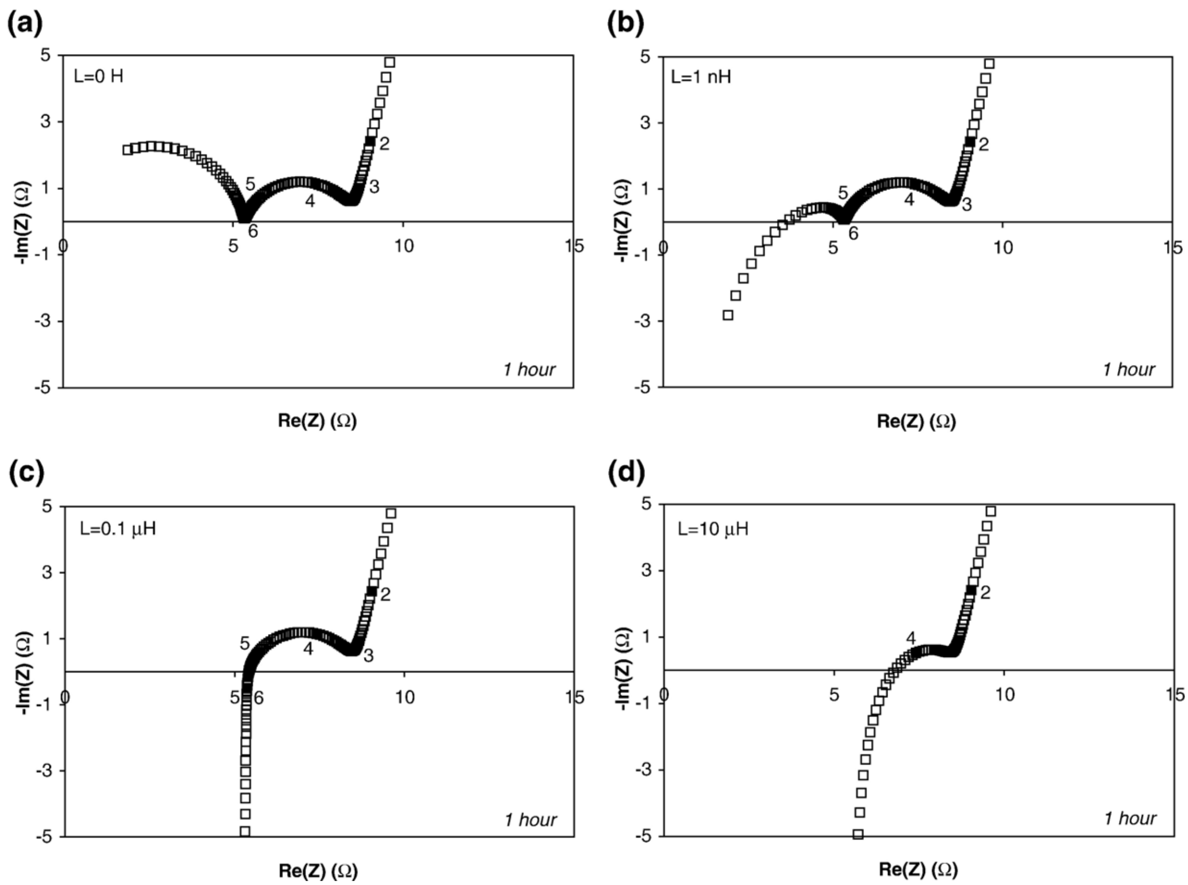

Fig. A.2. Simulated Nyquist plots for plain ordinary Portland cement (OPC) with 0.5 vol.% steel microfibers (~2 mm long and ~30 μm in diameter) at 1 h (see Fig. A.1) for varying amounts of inductance contributions; (a) no inductive contributions, (b) some inductive contribution (1×10^{-9} H), (c) moderate inductive contributions (1×10^{-7} H), and (d) large amounts of inductive contributions (1×10^{-5} H).

reliable *f*-function measurements can be obtained in fresh-cement FRCs, and that they change little upon set.

6. Conclusions

AC-impedance spectroscopy (AC-IS) is demonstrated to be an effective tool in non-destructive evaluation of fresh cement-based composites, before hardening, which allows for the direct monitoring of fiber dispersion during mixing and processing. The small electrical resistance values of fresh cement cause distortion of AC-IS derived data owing to parasitic inductive contributions from leads and cabling. Another electrical measurement technique, time domain reflectometry (TDR), which does not have the same limitations as AC-IS, is able to resolve the high-frequency behavior of the fresh cement-based composites. Using the two techniques together, the impedance/dielectric behavior can be investigated over a wide range of frequencies from 10^{-1} to 10^{9} Hz. Furthermore, TDR indicates that although the high-frequency bulk arc is not evident in the AC-IS data, information used for fiber dispersion can still be analyzed from the AC-IS derived Nyquist plots, since the inductive contributions are sufficiently small. However, for increasing amounts of inductance (e.g., lengthy cable runs, large electrode systems), the information from AC-IS might no longer be reliable (see Appendix). Comparison of fresh-cement composite data with hardened data confirm the ability of AC-IS to determine the parameters necessary for fiber dispersion analysis at early times.

Acknowledgements

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Appendix A

When using conventional impedance analyzers, although additional inductance effects (i.e., from cables, leads, etc.) distort the high-frequency bulk arc of highly conductive fresh cement paste, TDR demonstrates that the high-frequency cusp value remains valid and can be used for characterization (see Section 4). However, the AC-IS data may not produce a reliable high-frequency cusp (HF-cusp) value if inductance contributions increase and begin to alter more of the high-frequency data, which would eventually cause distortion of the HF-cusp value, R_{cusp}.

To evaluate the range over which the HF-cusp value can be evaluated with AC-IS derived Nyquist plots, equivalent circuit analysis was employed. Equivalent circuit modeling is a powerful tool in understanding the different mechanisms operating in a material system and how each mechanism contributes to the measured electrical properties at DC and at various AC frequencies [20,21]. The behavior of the entire composite system, which includes the composite material, interfaces, electroding, and machine contributions, can be described using circuit elements such as resistors (R), capacitors (C), constant phase elements (Q), and inductors (L). Previously, a universal equivalent circuit model was developed to understand composites exhibiting the "dual-cusp" behavior [14] (see Section 3.1). Details about equivalent circuit modeling and the universal equivalent circuit model are not given here, but can be found in the aforementioned references. To add the effect of the system inductance contributions, an inductor was added in series to the universal equivalent circuit model [19].

The measured Nyquist behavior of the fresh cement paste, with and without fibers, was fit using the "Equivalent Circuit" software program of Boukamp [21]. Details of the fitting procedure for the composite can be found elsewhere [19]. Fig. A.1 shows the simulated Nyquist data for plain cement, with and without 0.5 vol % steel microfibers that are ~2 mm long and ~30 μm in diameter tested at 1 h; the experimentally measured data are shown in Fig. 4b. The amount of inductance in series with the fresh paste cement and composite was found to be ~0.1 μH (microhenry).

Fig. A.2 shows the behavior of the simulated Nyquist plot for the composite (shown in Fig. A.1) as the inductance contribution was increased as shown. For large values of inductance, depression below the real axis causes a crossover point which differs increasingly from the true high-frequency cusp (HF-cusp) value, R_{cusp}. The Nyquist behavior of AC-IS data for fresh cement composites produced reliable HF-cusp values for inductance contributions less than $\sim 1^{-6}$ H. For comparison, owing to the larger resistance values of hardened cement composites, the upper limit for inductance contributions was found to be ~1 H. Likewise, for composites with smaller resistances than the fresh cement composite, the upper limit for inductance contributions would decrease as well. It should be stressed that this analysis should be conducted for each given application, taking into account the resistance of the fresh-cement composite, and the inductance contributions of the leads/cabling. Large structures with long lengths of cables/leads may be especially problematic.

References

[1] B. Mobasher, H. Stang, S.P. Shah, Microcracking in fiber-reinforced concrete, Cem. Concr. Res. 20 (1990) 665–676.

[2] A. Bentur, Fiber-reinforced cementitious materials, in: J. Skalny (Ed.), Materials Science of Concrete I, The American Ceramic Society, Inc., USA, 1989, pp. 223–284.

[3] N. Banthia, V. Bindiganavile, S. Mindess, Impact resistance of fiber reinforced concrete: a progress report, in: A.E. Naaman, H.W. Reinhardt (Eds.), Proceedings, 4th International RILEM Workshop on High Performance Fiber Reinforced Cement Composites (HPFRCC4), RILEM Publications, Ann Arbor, USA, 2003, pp. 117–131.

[4] N. Ozyurt, L.Y. Woo, B. Mu, S.P. Shah, T.O. Mason, Detection of fiber dispersion in fresh and hardened cement composites, Workshop on Improving the Performance of Concrete Through Science and Engineering, Electronic Proceedings of the March 2004 meeting (Evanston, IL), RILEM Publications, Bagneux, France, 2004.

[5] L.Y. Woo, S. Wansom, N. Ozyurt, B. Mu, S.P. Shah, T.O. Mason, Characterizing fiber dispersion in cement composites using ac-impedance spectroscopy, Cem. Concr. Comp. 27 (6) (2005) 627–636.

[6] L.Y. Woo, S. Wansom, T.O. Mason, N. Ozyurt, B. Mu, S.P. Shah, Ac impedance spectroscopy for nondestructive evaluation of fiber-reinforced cement composites, CONMAT '05, Third International Conference on Construction Materials: Performance, Innovations, and Structural Implications, Vancouver, Canada, August 22–24, 2005.

[7] W.J. McCarter, T.M. Chrisp, G. Starrs, J. Blewett, Characterization and monitoring of cement-based systems using intrinsic electrical property measurements, Cem. Concr. Res. 33 (2003) 197–206.

[8] C.A. Scuderi, T.O. Mason, H.M. Jennings, Impedance spectra of hydrating cement pastes, J. Mater. Sci. 26 (1991) 349–353.

[9] B.J. Christensen, T.O. Mason, H.M. Jennings, Influence of silica fume on the early hydration of portland cements using impedance spectroscopy, J. Am. Ceram. Soc. 75 (4) (1992) 939–945.

[10] P. Gu, P. Xie, J.J. Beaudoin, R. Brousseau, A.c. impedance spectroscopy (i): a new equivalent circuit model for hydrated portland cement paste, Cem. Concr. Res. 22 (5) (1992) 833–840.

[11] H.C. Kim, S.Y. Kim, S.S. Yoon, Electrical properties of cement paste obtained from impedance spectroscopy, J. Mater. Sci. 30 (1995) 3768–3772.

[12] D.E. MacPhee, D.C. Sinclair, S.L. Stubbs, Electrical characterization of pore reduced cement by impedance spectroscopy, J. Mater. Sci. Lett. 15 (1996) 1566–1568.

[13] N.E. Hager III, R.C. Domszy, Monitoring of cement hydration by broadband time-domain-reflectometry dielectric spectroscopy, J. Appl. Phys. 96 (9) (2004) 5117–5128.

[14] L.Y. Woo, S. Wansom, A.D. Hixson, M.A. Campo, T.O. Mason, A universal equivalent circuit model for the impedance response of composites, J. Mater. Sci. 38 (2003) 2265–2270.

[15] N.E. Hager III, Broadband time-domain-reflectometry dielectric spectroscopy using variable-time-scale sampling, Rev. Sci. Instrum. 65 (4) (1994) 887–891.

[16] B.J. Christensen, R.T. Coverdale, R.A. Olson, S.J. Ford, E.J. Garboczi, H.M. Jennings, T.O. Mason, Impedance spectroscopy of hydrating cement-based materials: measurement, interpretation, and application, J. Am. Ceram. Soc. 77 (11) (1994) 2789–2804.

[17] D.D. Edwards, J.H. Hwang, S.J. Ford, T.O. Mason, Experimental limitations in impedance spectroscopy: part v. Apparatus contributions and corrections, Solid State Ionics 99 (1997) 85–93.

[18] T.O. Mason, S.J. Ford, J.D. Shane, J.H. Hwang, D.D. Edwards, Experimental limitations in impedance spectroscopy of cement-based materials, Adv. Cem. Res 10 (4) (1998) 143–150.

[19] L.Y. Woo, Characterizing fiber-reinforced composite structures using ac-impedance spectroscopy (ac-is), Ph.D. thesis, Northwestern University, Evanston, IL (2005).

[20] J.R. Macdonald, Impedance Spectroscopy: Emphasizing Solid Materials and Systems, John Wiley and Sons, Inc., New York, 1987.

[21] B.A. Boukamp, Equivalent Circuit (Equivcrt. Pas), 1990.