High electric permittivity of polymer-
modified cement due to the capacitance of
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High electric permittivity of polymer-modified cement due to the capacitance of the interface between polymer and cement

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ABSTRACT

The electric permittivity is a material property that relates to the dielectric and electromagnetic behaviors. This work reports the effect of polymer admixtures on the permittivity (2 kHz) of cement paste. The permittivity is increased significantly by the addition of either methylcellulose (dissolved) or latex (styrene-butadiene, not dissolved), due to the capacitance of the interface between polymer and cement. The permittivity is effectively modeled by a material-level equivalent circuit model that comprises cement, polymer and cement/polymer interface in parallel. The series model is not effective. For both methylcellulose and latex, the cement and cement/polymer interface dominate the contributions to the permittivity, while the polymer contributes little. The contributions of polymer and cement/polymer interface increase monotonically with increasing polymer/cement ratio, while the contribution of cement decreases monotonically. Methylcellulose at the highest proportion of 1.4% by mass of cement gives permittivity 52, whereas latex at the highest solid latex proportion of 14% by mass of cement gives permittivity 43. For the same polymer/cement ratio, the permittivity is much higher for methylcellulose than latex. The difference between methylcellulose and latex is due to the much greater contribution of the cement/polymer interface to the permittivity for methylcellulose than latex, as caused by the nanoscale morphology of the methylcellulose and the consequent large cement/polymer interface area. At the same polymer/cement ratio, the fractional contribution from the cement/polymer interface is greater for methylcellulose than latex, though those from the polymer and cement are greater for latex than methylcellulose.
Introduction

The electric permittivity (the real part of the complex permittivity, also known as the dielectric constant) is a basic material property. It is a key to understanding the dielectric, ferroelectric, piezoelectric, pyroelectric, electric polarization and electromagnetic behaviors.

The piezoelectric behavior relates to the applications as strain/stress sensors (utilizing direct piezoelectric effect) and actuators (utilizing the converse piezoelectric effect) [1–4]. The pyroelectric behavior relates to the application as temperature and infrared sensors [5–7]. Due to the associated exchange interaction, ferroelectric behavior gives higher values of the permittivity than paraelectric behavior. A high value of the permittivity is attractive for providing high values of the piezoelectric coupling coefficient and pyroelectric coefficient. On the other hand, a low value of the permittivity is attractive for providing a high piezoelectric voltage coefficient.

The permittivity is also a key material property that governs the interaction of a material with electromagnetic radiation, such as radio wave. A high value of the permittivity is attractive for enhanced interaction with electromagnetic radiation, which is relevant to the use of electromagnetic radiation for nondestructive evaluation and object detection [8] and for electromagnetic interference (EMI) shielding [9–11].

The electric polarization behavior of a material affects the use of the electrical conductivity of the material, because the polarization causes a reverse electric field in the material [12, 13]. Furthermore, electric polarization is affected by stress, thus enabling polarization-based stress sensing [14]. The electrical conduction behavior relates to piezoresistivity-based strain/damage sensing [15–18], antistatic components [19], resistance-heating-based deicing [20, 21], electrical grounding and lightning protection. In addition, the conduction behavior relates to the cathodic protection of the steel embedded in concrete [22–25] and to the removal of ions (such as chloride ions) by electrochemical processes [25]. Although the electric permittivity is important for numerous functional properties, it has not been given adequate attention in the field of cement-based materials [6, 26–28]. The term “cement” refers to the hydrated cement throughout this paper, unless noted otherwise. Most prior work on the permittivity of cement-based materials concerns investigation of the process of hydration [29–32].

The relative permittivity of cement has been shown to be increased by latex addition [26, 33]. The addition to cement paste of latex (styrene–butadiene, 66% styrene, latex/cement mass ratio up to 0.30, where latex refers to the latex dispersion with 48 wt% latex solid) increases the relative permittivity at 2 kHz from 27 to 43. The increase occurs in spite of the low permittivity of latex solid compared to cement and is attributed to the interface between cement and latex solid [33]. The relative permittivity of silica fume cement has been shown to be increased from 21 to 54 at 10 kHz by the addition of short carbon fibers (0.5% by mass of cement, or 0.48 vol% of the cement paste) [26]. The relative permittivity of cement has been reported to be increased from 8 to 15 (1 kHz, 40 °C) by carbon nanofiber (1.2%) addition, such that the cement-based composite preparation unconventionally involves compaction of the cement mix [6].

Methylcellulose is a water-soluble polymeric admixture. The methylcellulose addition results in improved dispersion of the cement particles in the mix, in addition to a more uniform distribution of unhydrated cement particles in the matrix, such that there is no significant depletion near aggregate surfaces, thereby resulting in a reduction in the interfacial transition zone (ITZ) [34]. However, methylcellulose inhibits the hydration process of the cement clinker phases (such as C₃A) [35]. In particular, the addition of methylcellulose inhibits not only the formation of ettringite, but also the formation of monosulfate [36–38]. Methylcellulose addition causes the continued presence of gypsum after 24 h of hydration [36–38]. Moreover, the presence of methylcellulose results in a reduction in the reactivity of calcium sulfate dihydrate in the cement system [35]. In spite of an initial retardation of the hydration reactions, a higher degree of hydration is achieved with the presence of methylcellulose after 90 days of curing, due to the better dispersion of the cement particles in the water [39]. Methylcellulose (1% by mass of cement) addition results in a layered deposition of calcium hydroxide, arranged in stack without deformation, with polymer bridges between the layered calcium hydroxide crystals acting as a bonding agent between the layers, thereby improving the bonding and structure [36]. In addition, methylcellulose bridges between the layered crystals strengthen the microstructure [39]. Moreover,
methylcellulose causes the formation of polymer films [37]. As a consequence, methylcellulose addition provides a more cohesive microstructure, with a reduced amount of microcracks [34, 39, 40]. Furthermore, the methylcellulose polymer network reduces the porosity in relation to both large and fine pores [41].

The solubility of methylcellulose in water provides a method of forming nanoscale methylcellulose, which can have various morphologies that include the fibrillar morphology [40, 42]. This solubility is in contrast to the insolubility of latex particles [33] and is attractive for facilitating its dispersion in cement. Due to the insolubility in water, latex particles tend to agglomerate around the hydrating C3S grains and promote the formation of a composite microstructure [43]. The latex also tends to be adsorbed to the surfaces of cement particles, hydration crystals and other inorganic components [44–46], in addition to forming an interpenetrating network structure of latex and cement hydrate phases [47]. Furthermore, the latex retards the hydration in the early stage [48, 49]. The retardation is due to the sequestration of Ca\(^{2+}\) ions from the pore solution [50].

In the amount of 0.2–0.8% by mass of cement, methylcellulose addition increases the tensile strength, tensile ductility and compressive modulus, but decreases the tensile modulus, compressive strength and compressive ductility [51]. In addition, the addition of methylcellulose to cement paste containing silica fume enhances the viscous character of the resulting cured material, with the loss tangent increased by up to 50% and the storage modulus decreased by up to 14% [52]. Furthermore, the methylcellulose addition improves the bond strength between cement and stainless steel fiber [53], steel rebar [54] or carbon fiber [54] and enhances the dispersion of carbon fiber [55] and carbon nanofiber [56] in cement. Methylcellulose addition also decreases the thermal conductivity and increases the specific heat [57].

In spite of the above-mentioned prior work on the use of methylcellulose in cement-based materials, the effect of methylcellulose addition on the electric permittivity has not been previously reported. Due to the water-solubility of methylcellulose and the consequent polymer film formation [36, 39] and polymer network formation [41], the amount of interface between methylcellulose and cement is expected to be high (higher than that between latex and cement), thus leading to a high contribution of the interface to the electric permittivity.

Latex is much more commonly used in cement-based materials than methylcellulose. Latex-modified cement-based materials are attractive for their enhanced flexural strength [58–60], flexural toughness [60] and vibration damping ability [61], reduced void content [60] and improved adhesion and bonding properties [53, 62, 63]. However, the electrical behaviors of these materials have received little prior attention [60]. It has been reported that latex addition to cement increases both the electrical resistivity [60] and the electric permittivity [26]. The increase in resistivity is expected, since latex (a polymer) is an electrical insulator, while cement paste is conductive due to the ions present. However, the increase in electric permittivity is not expected, since the permittivity of latex (as typical for polymers) is lower than that of cement. It is reasonable to conjecture that polarization occurs at the interface between latex and cement, thereby causing the permittivity to be increased by the latex addition, as shown in our recent prior work [33].

The objectives of this work are (1) to investigate the effect of dissolved methylcellulose addition on the electric permittivity of cement, (2) to compare the effects of methylcellulose (dissolved, this work) and latex (not dissolved, prior work [33]), both as admixtures at various proportions, on the permittivity, (3) to understand the effects of methylcellulose and latex in terms of the contributions of cement, polymer and the interface between methylcellulose and cement on the permittivity, and (4) to provide a specimen-level equivalent circuit model to describe the electrical behavior of the polymer-modified cements.

**Experimental methods**

**Materials**

Portland cement (Type I, ASTM C150, unhydrated form) from Lafarge (Southfield, MI) is used. No aggregate is used. The water/cement mass ratio is fixed at 0.45, with the water including that in the latex dispersion in case that latex is used, and with the cement being that in the unhydrated form. Methylcellulose (Dow Chemical, Midland, MI, Methocel A15-LV) is used in the amount ranging
from 0.3 to 1.4% by mass of cement. A defoamer (Colloids, Inc., Marietta, GA, 1010) is used in the amount of 0.13 vol%, as in prior work [53–55, 57, 62], due to a small amount of bubbles generated by the addition of methylcellulose. Methylcellulose is first dissolved in water, and then, the defoamer is added and stirred by hand for 2 min.

The latex dispersion (#460NA, Dow Chemical, Midland, MI) has a styrene–butadiene copolymer with the polymer making up 48% of the dispersion mass and with the styrene and butadiene having a mass ratio of 66:34. An antifoaming agent (#2410, Dow Corning, Midland, MI) is used. The antifoam content is fixed at 0.5% by mass of latex dispersion. Firstly, the latex dispersion is mixed with the antifoam by hand for about 1 min. Secondly, the latex dispersion and water are mixed for 2 min.

The mix proportions for the case of latex are shown in Table 1. The mass ratio of the latex dispersion to cement ranges from 5.0 to 30.0%, whereas the mass ratio of the latex solid to cement ranges from 2.4 to 24.4%. As shown in Table 2, the mass ratio of methylcellulose to cement ranges from 0.3 to 1.4%. The volume fractions of the constituents (cement paste and polymer solid) are shown in Table 2 for both latex and methylcellulose.

The above-mentioned mixing is conducted using a rotary (Hobart) mixer with a flat beater. After the mixing, cement and water are added and further mixing is conducted for 5 min. Then, the mixture is poured into an oiled mold of dimensions 25 mm × 25 mm, immediately followed by covering the content of the mold with a wet towel in order to prevent loss of water. The specimens are demolded after 1 day and cured in air at room temperature (relative humidity = 100%) for the next 27 days.

Before capacitance measurement, the samples are burnished with water to ensure that the surfaces are smooth. No damage is caused by the burnishing. All three orthogonal dimensions are separately measured for each specimen after the burnishing.

### Permittivity measurement and analysis method

Each specimen tested is a square of dimensions 25 mm × 25 mm, with thickness ranging from about 2 mm to about 4 mm. The aspect ratio is large enough for the fringing field to be small enough, so that the permittivity determination is reliable, as shown in the prior work of this research group [27].

The permittivity is measured using the parallel-plate capacitor geometry, with two electrical contacts sandwiching the specimen symmetrically. An electrical contact (copper foil of thickness 0.15 mm) covers the entire area of each of the two square surfaces of the specimen. Between each of the two copper foils and the specimen is positioned an electrically insulating Teflon-coated glass fiber composite film (thickness 58 µm, relative permittivity 1.5 at 2 kHz). The configuration is illustrated in Fig. 1. The importance of using an insulating film has been noted previously [64]. Instead of using an insulating film, an air gap of 0.25 mm has also been used in prior work [65]. However, an air gap is associated with a very large resistance, so that the electric field experienced by the cement specimen would become too small for adequate capacitance measurement. In fact, it is important for the insulating film to be thin enough, so that the resistance is not too high. A pressure of 9.93 kPa is applied in the direction perpendicular to the plane of the sandwich.

The capacitance is measured using a precision RLC meter (Instek LCR-816 High Precision LCR Meter, 100 Hz–2 kHz), with the electric field across the thickness of the specimen fixed at 0.10 V/mm. The voltage is increased with the specimen thicknesses; for example, for a specimen thickness of 3.90 mm, the

### Table 1 Mix proportions for the latex-modified cement-based materials studied

<table>
<thead>
<tr>
<th>Latex dispersion/cement mass ratio</th>
<th>Latex solid/cement mass ratio</th>
<th>Cement (g)</th>
<th>Latex dispersion (g)</th>
<th>Water (g)</th>
<th>Antifoam (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100.0 ± 0.5</td>
<td>0</td>
<td>45.0 ± 0.05</td>
<td>0</td>
</tr>
<tr>
<td>0.05</td>
<td>0.024</td>
<td>100.0 ± 0.5</td>
<td>5.0 ± 0.5</td>
<td>42.4 ± 0.05</td>
<td>0.025</td>
</tr>
<tr>
<td>0.10</td>
<td>0.048</td>
<td>100.0 ± 0.5</td>
<td>10.0 ± 0.5</td>
<td>39.8 ± 0.05</td>
<td>0.050</td>
</tr>
<tr>
<td>0.15</td>
<td>0.072</td>
<td>100.0 ± 0.5</td>
<td>15.0 ± 0.5</td>
<td>37.2 ± 0.05</td>
<td>0.075</td>
</tr>
<tr>
<td>0.20</td>
<td>0.096</td>
<td>100.0 ± 0.5</td>
<td>20.0 ± 0.5</td>
<td>34.6 ± 0.05</td>
<td>0.100</td>
</tr>
<tr>
<td>0.25</td>
<td>0.120</td>
<td>100.0 ± 0.5</td>
<td>25.0 ± 0.5</td>
<td>32.0 ± 0.05</td>
<td>0.125</td>
</tr>
<tr>
<td>0.30</td>
<td>0.144</td>
<td>100.0 ± 0.5</td>
<td>30.0 ± 0.5</td>
<td>29.4 ± 0.05</td>
<td>0.150</td>
</tr>
</tbody>
</table>
voltage is 0.39 V. The frequency used is 2 kHz, because it is the highest frequency provided by the LCR meter used. Lower frequencies give consistent results, though the results are clearest at the highest frequency. The capacitance reported here is for the equivalent electrical circuit of a capacitance and a resistance in parallel.

The methodology for measuring the capacitance involves firstly the separation of the interfacial capacitance (interface between the specimen and an electrical contact) from the volumetric capacitance (the volume of the specimen). This decoupling is enabled by the testing of three different thicknesses of the sandwiched specimen and plotting the inverse of the measured capacitance \( C_m \) versus thickness \( l \). The slope of the straight-line plot is equal to \( 1/(\kappa \varepsilon_0 A) \), where \( \kappa \) is the relative permittivity of the specimen, \( \varepsilon_0 \) is the permittivity of free space, and \( A \) is the area of the sandwiched dielectric material. Hence, \( \kappa \) is obtained from the reciprocal of the slope. The intercept of the straight with the vertical axis at zero thickness equals \( 2/C_i \), where \( C_i \) is the capacitance of one interface. In other words,

\[
1/C_m = 1/C_v + 2/C_i, \tag{1}
\]

where \( C_v \) is the volumetric capacitance. Using Eq. (1), which is based on capacitors in series, \( 1/C_v \) is obtained for a given value of \( l \). The \( C_v \) is given by

\[
C_v = \varepsilon_0 \kappa A/l, \tag{2}
\]

where \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ F/m}) \), \( A \) is the area of the sandwich (i.e., the area of the electrical contact), and \( l \) is the thickness of the specimen sandwiched by the electrical contacts.

The cement, polymer (methylcellulose or latex) solid and the interface between these components are modeled electrically as continuous dielectric components that are either in parallel or in series, with capacitances \( C_C \), \( C_P \) and \( C_I \), respectively. This dielectric continuity assumption is consistent with the results of prior work on the film and network structure of cement containing methylcellulose [54, 58] and is supported by the previously reported nanoscale fibrillar morphology of the methylcellulose.
With the cement and polymer solid components alternating in their positions (Fig. 2), let \( N \) be the number of cement layers. Then, the number of polymer solid layers is \( N - 1 \) and the number of cement/polymer interfaces is \( 2N - 2 \).

In the specimen-level parallel model (Fig. 2a), according to the rule of mixtures [66],

\[
C_v = NC_C + (N-1)C_P + (2N-2)C_I. \tag{3}
\]

Rearrangement of Eq. (3) and the use of Eq. (2) give the contribution \( \kappa_I \) of the interfaces to the relative permittivity of the cement-based material as

\[
\kappa_I = (2N-2) \frac{C_I}{A \varepsilon_0} = \kappa - \frac{V_C}{\kappa_C} - \frac{V_P}{\kappa_P}, \tag{4}
\]

where \( V_C \) and \( \kappa_C \) are the volume fraction and relative permittivity of cement, respectively, and \( V_P \) and \( \kappa_P \) are the volume fraction and relative permittivity of the polymer solid, respectively. The terms \( V_C \kappa_C \) and \( V_P \kappa_P \) are the contributions of the cement and polymer solid to the relative permittivity of the cement-based material, respectively. The volume fractions are obtained from the mass fractions and the densities.

The density of cement is taken as 1.62 g/cm\(^3\), which is the density of the cement-based material without polymer addition, as measured in this work.

For the methylcellulose solid, the density is 1.39 g/cm\(^3\) [67] and the relative permittivity is 3.0 [68]. The density of latex solid (with 66% styrene) is taken as 0.994 g/cm\(^3\), which is obtained by extrapolating the known densities of styrene–butadiene of 0.965 g/cm\(^3\) at 45% styrene and 0.910 g/cm\(^3\) for 5% styrene [69]. The relative permittivity of styrene–butadiene solid is 2.8 [70].

In the specimen-level series model (Fig. 2b), according to the rule of mixtures [66],

\[
\frac{1}{C_v} = N/C_C + (N-1)/C_P + (2N-2)/C_I. \tag{5}
\]

Rearrangement of Eq. (5) and the use of Eq. (2) give the contribution \( 1/\kappa_I \) of the interfaces to the reciprocal of the relative permittivity of the cement-based material as

\[
\frac{1}{\kappa_I} = (2N-2) \frac{A \varepsilon_0}{C_I} = \frac{1}{\kappa} - \frac{V_C}{\kappa_C} - \frac{V_P}{\kappa_P}. \tag{6}
\]

The terms \( V_C / \kappa_C \) and \( V_P / \kappa_P \) are the contributions of the cement and polymer solid to the reciprocal of the relative permittivity of the cement-based material, respectively.

This work uses a technique which differs greatly from the widely used technique of impedance spectroscopy, which measures the impedance as a function of frequency and uses the frequency dependence to obtain information. Firstly, the technique of this work does not measure the impedance, but measures the relative permittivity (the real part of the permittivity). In connection with permittivity measurement, this work measures the capacitance with a test configuration in which an insulating film is positioned between the specimen and each of the two electrodes. The presence of this film ensures that the resistance of the system is high enough for the measured capacitance given by the LCR is correct. However, the presence of this film would cause the specimen resistance to be not effectively measured. Resistance measurement is not a part of this study. An insulating film is not usually used in impedance spectroscopy, thus causing the capacitance measurement in the impedance spectroscopy to be questionable. Second, the technique of this work decouples the contribution of the specimen–contact interface from the contribution of the volume of the specimen, as achieved by testing specimens of the same type at three different thicknesses and plotting the reciprocal of the measured capacitance versus the thickness (Fig. 3). The slope of this plot relates to the
permittivity of the specimen, with the specimen–contact interface contribution to the measured capacitance removed. This decoupling is not adequately performed in impedance spectroscopy, as explained below. Thirdly, the technique of this work uses a system-level equivalent circuit model (Fig. 4, which is drawn for the case of the specimen-level parallel model shown in Fig. 2a) that includes the specimen and the two electrical contacts and reflects the testing configuration, in which the specimen is in series with two electrical contacts on its two sides, such that each of the specimen and electrical contacts consists of a resistance and a capacitance in parallel. This system-level circuit model is intended to explain the method of testing rather than the method of analysis. The testing includes the decoupling of the specimen contribution and the contact contribution and also includes having the LCR meter set for resistance and capacitance in parallel. In this work, only the volumetric and contact capacitances in the system-level model are measured; the volumetric and contact resistances are not measured. None of the values of the circuit elements is obtained by calculation, but the values are obtained by direct measurement. Fourthly, the technique of this work does not need to address the frequency dependence in order to obtain meaningful information. In contrast, impedance spectroscopy is focused on the frequency dependence of the impedance, as conventionally described in terms of the Nyquist plot, for the purpose of deriving by mathematical fitting of the plot an equivalent electrical circuit that is intended to describe the electrical/dielectric behavior of the material. The system-level circuit model obtained by the curve fitting [71] tends to be not unique, so the determined values of the circuit elements (including the interfacial and volumetric elements) in the model are not very meaningful [72, 73].

**Results and discussion**

**Effect of methylcellulose on the permittivity**

Figure 3 shows that the experimental plot of $1/C_m$ versus $l$ is indeed linear, as observed for all of the cement-based materials studied. Table 3 shows that the relative permittivity $\kappa$ of the cement-based material increases monotonically with increasing methylcellulose/cement ratio. The value is increased from 27 (for the absence of methylcellulose) to 52 (for the highest methylcellulose/cement ratio of 0.012). The value of 27 for the absence of methylcellulose is in agreement with prior work [26, 33]. Linearity is obtained for all the polymer-modified cement-based materials of this work, whether the polymer is methylcellulose or latex.

**Comparison of the effects of methylcellulose and latex on the permittivity**

Latex is a commonly used polymeric admixture that is not soluble in water. The effect of latex (styrene–butadiene copolymer) addition on the permittivity...
has been addressed in our prior work [33]. This section compares the effects of dissolved methylcellulose (this work) and undissolved latex (prior work) on the permittivity. For both methylcellulose and latex, the polymer in the polymer/cement mass ratio refers to the polymer solid. This is in contrast to our prior work on latex [33], which uses the mass of the latex particle water-based dispersion in the latex/cement ratio. The highest polymer/cement ratio used in the study is much higher for latex than methylcellulose, in accordance with the common ranges of this ratio used in prior work for these two polymeric admixtures [36, 41, 55].

As shown in Fig. 5, for both methylcellulose and latex, the relative permittivity increases monotonically with increasing polymer/cement ratio. At the same polymer/cement ratio, the relative permittivity is much higher for methylcellulose than latex. Even at the highest latex/cement ratio of 0.14, the relative permittivity (43) is lower than the value (52) for the highest methylcellulose/cement ratio of 0.012. The high values of the relative permittivity for methylcellulose can be understood through material-level modeling of the permittivity using the parallel model of the rule of mixtures, as described below in terms of both the parallel model and the series model.

As shown in Fig. 6a, the contribution of the cement matrix to the measured relative permittivity, according to the material-level parallel model, decreases with increasing polymer/cement ratio for both methylcellulose and latex, as expected. The data for the two polymers lie essentially on the same

Table 3: Effect of the methylcellulose/cement ratio on the relative permittivity of the cement-based material

<table>
<thead>
<tr>
<th>Ratio</th>
<th>0</th>
<th>0.004</th>
<th>0.005</th>
<th>0.006</th>
<th>0.007</th>
<th>0.009</th>
<th>0.010</th>
<th>0.011</th>
<th>0.012</th>
<th>0.013</th>
<th>0.014</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$</td>
<td>26.98±0.85</td>
<td>31.13±0.78</td>
<td>33.49±0.74</td>
<td>36.16±0.89</td>
<td>37.66±0.74</td>
<td>42.03±0.89</td>
<td>43.76±0.74</td>
<td>46.36±0.89</td>
<td>48.86±0.74</td>
<td>50.22±0.74</td>
<td>51.65±0.89</td>
</tr>
</tbody>
</table>

Figure 5: Effect of the polymer/cement mass ratio on the measured relative permittivity $\kappa$. Open square: methylcellulose. Filled circle: latex.
As shown in Fig. 6b, the contribution of the polymer to the measured relative permittivity, according to the material-level parallel model, increases with increasing polymer/cement ratio for both methylcellulose and latex, as expected. The data for the two polymers lie essentially on the same curve, supporting the effectiveness of the material-level parallel model. Due to the low values of the methylcellulose/cement ratio compared to the latex/cement ratio, the contribution of the polymer is lower for methylcellulose than latex.

As shown in Fig. 6c, the contribution of the cement/polymer interface to the measured relative permittivity, according to the material-level parallel model, increases with increasing polymer/cement ratio for both methylcellulose and latex, as expected. The data for the two polymers lie on different curves, with the slope of the curve for methylcellulose being higher than that for the curve for latex. Furthermore, the highest value for methylcellulose is above that for latex, in spite of the low methylcellulose content. These results mean that methylcellulose is more effective than latex for providing cement/polymer interface that enhances the permittivity of the cement-based material. In other words, even at a lower value of the polymer/cement ratio, methylcellulose provides comparable or greater interface-induced permittivity than latex. This is attributed to the nanostructure of the methylcellulose and the consequent large area of the cement/polymer interface per unit volume.

The fractional contributions of the cement, polymer and cement/polymer interface to the permittivity are shown in Fig. 7. Figure 7a shows that the fractional contribution of the cement is comparable for methylcellulose and cement. The highest value for methylcellulose is higher than that of latex. These occur though the polymer/cement ratio is much lower (i.e., the cement/polymer ratio is much higher) for methylcellulose than latex. Extrapolation of the curve for latex to lower values of the polymer/cement ratio suggests that, at the same polymer/cement ratio, the fractional contribution of the cement is greater for latex than methylcellulose. This means that the cement is a less efficient contributor in the presence of methylcellulose than in the presence of latex. This difference between methylcellulose and latex is probably due to the nanostructure of methylcellulose and the consequent reduced degree
of dielectric continuity of the cement caused by the distributed nanoscale methylcellulose.

Figure 7b shows that the fractional contribution from the polymer is much lower for methylcellulose than latex. Extrapolation of the curve for latex to lower values of the polymer/cement ratio suggests that, for the same polymer/cement ratio, the fractional contribution from the polymer is greater for latex than methylcellulose.

Figure 7c shows that the fractional contribution from the cement/polymer interface is comparable for methylcellulose and latex, in spite of the much smaller polymer/cement ratio for methylcellulose than latex. Extrapolation of the curve for latex to lower values of the polymer/cement ratio suggests that, for the same polymer/cement ratio, the fractional contribution from the interface is greater for methylcellulose than latex. This difference between methylcellulose and latex is probably due to the nanostructure of the methylcellulose and the consequence large area of the cement/polymer interface for methylcellulose. Hence, the superior effectiveness of methylcellulose compared to latex for increasing the permittivity (Fig. 5) is due to the cement/polymer interface.

Figure 8 shows the effect of the polymer/cement mass ratio on the contributions of the cement, polymer and cement/polymer interface to the reciprocal 1/\( \kappa \) of the measured relative permittivity, according to the material-level series model. The contribution 1/\( \kappa_i \) of the interface between cement and polymer, as shown in Fig. 8c, is negative. The negative value is not reasonable, indicating the seriously inadequate effectiveness of the material-level series model. Nevertheless, the contribution of the cement decreases with increasing polymer/cement ratio, and the contribution of the polymer increases with increasing polymer/cement ratio, as in Fig. 7, which is obtained by using the material-level parallel model. The inadequate effectiveness of the material-level series model may stem from the fact that the permittivity is measured along the thickness (shortest dimension) of the specimen and the greater chance for the polymer films to be tortuously dielectrically continuous along this short dimension than along the long dimension perpendicular to the thickness direction, even if the polymer films are randomly oriented. In other words, the chance of attaining a tortuously dielectrically continuous path is higher when the distance over which dielectric continuity is required is shorter.

The parallel and series material-level models are the two most basic material-level models for calculating the relative permittivity of a composite material. Both material-level models have been
Figure 8 Effect of the polymer/cement mass ratio on the contributions to the reciprocal $1/\kappa$ of the measured relative permittivity, according to the material-level series model (Fig. 2b). a The contribution $V_C/\kappa_C$ of the cement. b The contribution $V_P/\kappa_P$ of the polymer. c The contribution $1/\kappa_I = (2N - 2)\frac{\sigma}{e_0 A_C I_l}$ of the interface between cement and polymer. Open square: methylcellulose. Filled circle: latex.
investigated in this work, but the material-level parallel model is found to give more meaningful results than the material-level series model. Both material-level models assume dielectric continuity of the constituents, i.e., cement, polymer and the cement/polymer interface. A degree of dielectric continuity of the polymer is supported by the previously reported polymer film formation in a cement-based material [54]. More accurately, the calculated value of the permittivity should be taken as being bound by the calculated value based on the material-level parallel model and that based on the material-level series model [74]. However, the former value alone is used in this work, due to the seriously inadequate effectiveness of the material-level series model and the above-mentioned higher chance of attaining a tortuously dielectrically continuous path in the measurement direction of shorter distance than the transverse direction of much longer distance.

The superior effectiveness of methylcellulose compared to latex for increasing the permittivity of cement is consistent with the superior effectiveness of methylcellulose compared to latex for increasing the vibration damping ability [56], bond strength of cement with steel [36] and degree of carbon fiber dispersion [39], and for decreasing the thermal conductivity [41]. Methylcellulose in the amount of 0.4% by mass of cement is comparable to latex in the amount of 20% by mass of cement in the effectiveness for enhancing the vibration damping ability of cement [56]. Methylcellulose in the amount of 0.8% by mass of cement is comparable to latex in the amount of 25% by mass of cement in the effectiveness for decreasing the thermal conductivity of cement [41]. Methylcellulose in the amount of 0.4% by mass of cement is better than latex in the amount of 20% by mass of cement in the effectiveness for enhancing the degree of carbon fiber dispersion in cement [39]. In addition, methylcellulose in the amount of 0.4% by mass of cement is comparable to latex in the amount of 20% by mass of cement in the effectiveness for enhancing the bond strength of cement to steel fiber [36].

**Conclusion**

This work provides the effect of polymer admixtures on the electric permittivity (2 kHz) of cement paste. The measurement involves measuring the capacitance of specimens of three thicknesses for each composition, so that the contributions of the specimen and the interface between the specimen and each electrical contact are decoupled. For every composition, the curve of 1/C (where C is the measured capacitance) versus thickness is linear.

The permittivity is increased significantly by the addition of either methylcellulose (dissolved) or latex (styrene–butadiene, not dissolved) to cement paste, due to the capacitance of the interface between polymer and cement. The permittivity is effectively modeled in the material level by an equivalent circuit model that comprises cement, polymer and cement/polymer interface in parallel. The material-level series model is not effective. For both methylcellulose and latex, cement and the cement/polymer interface dominate the contributions to the permittivity, while the polymer contributes much less. The contribution of polymer to the permittivity and that of the cement/polymer interface increase monotonically with increasing polymer/cement ratio, while the contribution of cement decreases monotonically.

For the same polymer/cement ratio, the permittivity is much higher for methylcellulose than latex. Methylcellulose at the highest proportion of 1.4% by mass of cement gives permittivity 52, whereas latex at the highest solid latex proportion of 14.4% by mass of cement gives permittivity 43.

The difference between methylcellulose and latex in their effects to the permittivity is due to the much greater contribution of the cement/polymer interface to the permittivity for methylcellulose than latex, as caused by the nanoscale morphology of the methylcellulose and the consequent large cement/polymer interface area. At the same polymer/cement ratio, the fractional contribution from the cement/polymer interface is greater for methylcellulose than latex, though the fractional contribution from the polymer is greater for latex than methylcellulose, and the fractional contribution of the cement is greater for latex than methylcellulose.

The superior effectiveness of methylcellulose compared to latex for increasing the permittivity of cement is consistent with the superior effectiveness of methylcellulose compared to latex for increasing the vibration damping ability [56], bond strength of cement with steel [36] and degree of carbon fiber dispersion [39], and for decreasing the thermal conductivity [41].
Compliance with ethical standards

Conflict of interest  The authors declare that they have no conflict of interest.

References


