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Effect of Styrene-butadiene Rubber on the Electrical Properties of Carbon Black/Cement Mortar

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Highlights

- Styrene-butadiene rubber (SBR) was used to modify CB/PC mortar.
- The piezoresistivity effect of mortars increased with the increase of SBR content.
- Both positive and negative piezoresistivity occurred in mortars during compression.
- The piezoresistivity mechanism was explained in terms of both the tunneling effect and capacitance effect

Abstract: The piezoresistivity of carbon black/cement mortar (CB/PC) makes it a potential candidate for the development of smart structure with sensing capability. To ensure reliable sensing results in different environments, a hydrophobic styrene-butadiene rubber (SBR) was incorporated to reduce the effect of moisture on the piezoresistivity. The influence of SBR content (0, 5, 10 and 15 wt.%) on the electric conductivity and piezoresistivity of SBR/CB/PC mortar with different moisture content was experimentally studied. Results indicate that the electric conductivity and piezoresistivity effect of SBR/CB/PC mortars increase with increasing SBR content. Also, compared to pure CB/PC mortars, the electrical

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properties of SBR/CB/PC mortars were significantly less sensitive to the variation of moisture. Under cyclic loading, both positive (PP) and negative piezoresistivity (NP) are found to occur in SBR/CB/PC mortars. This behavior can be explained in terms of a mechanism with both the tunneling effect and capacitance effect between CB particles during compression.

Keywords: Electrical properties; Positive piezoresistivity; Negative piezoresistivity; Cement mortar; Styrene-butadiene rubber

1. Introduction

Portland cement (PC) exhibits piezoresistivity and can be potentially developed into a self-sensing material for damage detection, interfacial properties characterization and other non-destructive monitoring. Various studies in the literature have shown that the addition of an appropriate amount of carbon black (CB) can enhance both the strength and piezoresistivity of PC.\textsuperscript{1-8} However, PC (with or without CB) is a hydrophilic material with high hygroscopicity, leading to large variation of its piezoresistivity with the change in humidity of the surrounding environment.\textsuperscript{5,8} Moreover, CB is a lightweight material (density of about 0.70-0.8 g/cm\textsuperscript{3}), which usually form agglomerates at the interface of sand aggregates or moves to the upper layer of CB/PC samples when vibration is applied for compaction. The resulting inhomogeneity will weaken the mechanical performance. To address the above issues, a feasible method is to apply a hydrophobic polymer which can (i) reduce the amount of moisture that can penetrate into the material, and (ii) enclose the CB particles to prevent their segregation from the rest of the matrix.

Due to the high fracture elongation of the copolymer styrene–butadiene rubber (SBR), it has been widely used in the modification of cement materials.\textsuperscript{9-12} Common applications of SBR-modified cement composites range from concrete bridge deck overlays, lining for sewer lines, floors for parking structures and other structural applications such as machinery
foundation and utility structures. SBR-modified cement composites have high tensile strength, good ductility and high impact resistance due to the formation of three-dimensional polymer network throughout the hardened cementitious material. Because of the void-sealing effect of this network and its bridging across cracks, the porosity decreases and pore radius of cementitious matrices are refined. Furthermore, the transition zone may be improved due to the adhesion effect of the polymer. Water absorption can hence be significantly reduced. Based on the beneficial effects of SBR in PC, a new cement-based piezoelectric material containing a hybrid of SBR and CB is designed and studied. The main objective of this paper is to understand and characterize the influence of SBR content on both the electric conductivity and piezoresistivity of SBR/CB/PC composites with different moisture contents.

2. Experimental program

2.1 Materials

The cementitious material used in the test was ordinary Portland cement. Its chemical composition and physical properties are shown in Table 1. The fine aggregate was natural standard sand with a specific gravity of 2.62. Carbon black was provided by Shandong Zibo Guanghua-Technology Company (Limited) in China. The properties are given in Table 2. The Superplasticizer (SP) was a liquor of phenolic aldehyde, with a solid content of 31% and a density of 1.1 g/cm$^3$. The employed Styrene Butadiene Rubber emulsion (SBR), provided by Shanghai BSF Technology Company (Limited), was a fluid milk-white solution with solid content of 48% and density of 1.09 g/cm$^3$.

Table 1. Chemical and physical properties of Cement

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>LOI</th>
<th>Specific surface, Blaine, m$^2$.Kg$^{-1}$</th>
<th>Compressive strength, 28-day, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.2</td>
<td>8.4</td>
<td>2.1</td>
<td>64.8</td>
<td>2.5</td>
<td>2.8</td>
<td>1.2</td>
<td>367</td>
<td>46.8</td>
</tr>
</tbody>
</table>
Table 2. Properties of carbon black

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Specific surface area (m²/g)</th>
<th>Apparent density (g/cm³)</th>
<th>Resistivity (Ω.cm)</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-40</td>
<td>550</td>
<td>0.7~0.8</td>
<td>0.75</td>
<td>7.6</td>
</tr>
</tbody>
</table>

2.2 Preparation of specimens

Four mixes of cement-based mortars were prepared for the piezoresistivity and electric conductivity test. The mix proportions of these composites are shown in Table 3. SP was added at the amount of 0.5% by weight of cement. In the cases of SB/PC composites (CBPCa), the cement, SB, sand, water and water-reducing agent were all mixed in a rotary mixer with a flat beater for 5 minutes. In the cases of the cement mortar containing SBR (CBPCb, CBPCc, CBPCd), CB and SBR were firstly mixed by mean of ultrasonic vibration to achieve a better dispersion of CB within the SBR. Meanwhile, cement, sand and water-reducing agents were pre-mixed for 3 minutes. Then, the uniformly dispersive mixture of SBR/CB and water were added to the pre-mixed cement mortar in a rotary mixer, where all the ingredients are further mixed for 5 minutes.

Table 3. Mix proportions of SBR/CB/PC mortars

<table>
<thead>
<tr>
<th>Cement</th>
<th>SBR */ %</th>
<th>CB */ %</th>
<th>Sand</th>
<th>SP */ %</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBPCa</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>CBPCb</td>
<td>1</td>
<td>5</td>
<td>0.5</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>CBPCc</td>
<td>1</td>
<td>10</td>
<td>0.5</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>CBPCd</td>
<td>1</td>
<td>15</td>
<td>0.5</td>
<td>2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*: given as percent of cement content by mass

After cement mortar is poured into oiled molds (40×40×160mm), electrical contacts were
applied by embedding 4 pieces of small copper strips along the length of the specimen, as shown in Fig.1, and an electric vibrator was used to obtain a better compaction. The specimen surface was then smoothened, and covered with wet clothes. All specimens were demolded 1 day after casting. Thereafter, they were cured in water at a constant room temperature (of 25±2°C) up to 7-day age and then cured in air until the time of testing.

![Samples and instrument used in the piezoresistivity test](image)

**Figure 1. Samples and instrument used in the piezoresistivity test**

### 2.3 Resistance and piezoresistivity measurement

Electrical resistance measurement of cement mortars with 28-day age was performed with a four-probe method (Fig.1). Before testing, all specimens were dried in a high temperature drying oven at 60°C for 24 hours. Six specimens for each mix proportion were tested in this study. The instrument used in the piezoresistivity test was 34401A Digital multimeter. Electrical resistivity $\rho_v$ of each specimen was obtained from the measured volume resistance $P_v$. The relationship between the electrical resistivity $\rho_v$ and the volume resistance $P_v$ is as follows:
\[
\rho_v = \left( \frac{A}{L} \right) \times P_v
\]  

(1)

where \( A \) is the embedded area of copper strip in the composites and \( L \) is the length between two inner electrical contacts.

The piezoresistivity test was carried out as follows: Cyclic compressive loading was applied with a universal testing machine at a displacement rate of 0.50 mm/min. The minimum and maximum compressive loading were 0 kN and 15 kN (corresponding to applied stress of 0 MPa and 3.75 MPa). All of the measurements were automatically recorded through a data logger. The piezoresistivity of each sample was calculated by the following equation:

\[
\Delta R = \left( \frac{R_\sigma - R_0}{R_0} \right) \times 100\%
\]  

(2)

In eqn(2), \( R_\sigma \) is the resistance under stress \( \sigma \) while \( R_0 \) is the resistance when no stress is applied. After the testing describe above, in order to investigate the influence of moisture content on the piezoresistivity of SBR/CB/PC composites, all specimens were further dried at 60°C for another 24 hours before another electrical resistance and piezoresistivity test (2\textsuperscript{nd} test in Table 4) was carried out.

2.4 Scanning electron microscope (SEM) analysis

The morphology and microstructure of the fractured surfaces of both CB/PC and SBR/CB/PC composites were observed using a Quanta 200 field emission environmental scanning electron microscope. Samples were kept in alcohol and dried in a vacuum-drying oven at 80°C for 24h, and the surfaces to be inspected were gold coated before examination.

3. Results and discussion

3.1 Electrical properties

According to Cao et al., the time for polarization saturation of cementitious composites
is about 100s while the completion of the depolarization takes around 1000s.\textsuperscript{15} In order to eliminate the effect of electric polarization and depolarization on all specimens, the resistance value measured at 1000s was chosen as the initial resistance for each specimen.\textsuperscript{16} The test results of electrical resistivity and piezoresistivity of cement mortars with different SBR are shown in Table 4.

**Table 4. Electrical properties of cement mortars with different SBR content**  
(PP= Positive piezoresistivity, NP= Negative piezoresistivity)

<table>
<thead>
<tr>
<th></th>
<th>1\textsuperscript{st} test (after first drying)</th>
<th>2\textsuperscript{nd} test (after additional drying)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average mass/ g</td>
<td>Resistivity/ ohm.cm</td>
</tr>
<tr>
<td>CBPCa</td>
<td>567.5</td>
<td>5800</td>
</tr>
<tr>
<td>CBPCb</td>
<td>550.2</td>
<td>5000</td>
</tr>
<tr>
<td>CBPCc</td>
<td>538.9</td>
<td>3600</td>
</tr>
<tr>
<td>CBPCd</td>
<td>523.7</td>
<td>2700</td>
</tr>
</tbody>
</table>

\textsuperscript{a}N/P Ratio\textsuperscript{a} given as the number of samples with NP behavior over PP behavior

As shown in Table 4, the volume electrical resistivity decreased with the increase of SBR content. Specifically, the volume electrical resistivity of CBPCa, CBPCb, CBPCc and CBPCd were about 5800, 5000, 3600 and 2700 ohm.cm, respectively. A plausible explanation is that the contact points of CB particles increase with the increase of SBR content. This is because SBR can seal the pores of cement matrix, hence preventing the agglomeration of CB particles in the pores. The effective CB content in the matrix, which can form conductive pathways, is therefore increased. As demonstrated by SEM (Fig.2), a large amount of CB particles were aggregated in the pores of CBPCa. On the other hand, in CBPCd, CB particles coated by SBR film were homogeneously distributed in the cement matrix.
mortar. Moreover, the increase of SBR content facilitates the formation of three-dimensional networks which are effective in increasing the conductive pathways. As a result, the volume electrical resistivity of SBR/CB/PC mortar decreases with the increase of SBR content.

![Typical SEM images of the fractured surface of CBPCa and CBPCd.](image)

(a1, a2) CB particles aggregated in the pore of PC mortar

(b1,b2) The uniform distribution of CB particles warped by SBR film

**Figure. 2 Typical SEM images of the fractured surface of CBPCa and CBPCd.**

From Table 4, after additional drying in an oven at 60°C for 24 hours, the mass losses of CBPCa, CBPCb, CBPCc and CBPCd were measured to be 2.8%, 1.9%, 1.5% and 0.8%, respectively. The mass losses were mainly due to the evaporation of water. The reduced mass losses with increasing SBR content can be explained in terms of the variation of total water
content in the various samples. The hydrophilic feature of cement mortars varies with the variation of SBR content. With higher SBR content, the cement mortar becomes less hydrophilic and lower in hygroscopicity. As a result, less water will be absorbed after curing in the same environment. At the same time, as the pore-sealing effect of SBR refines the pore size and decreases the porosity of mortars, the total water content is further reduced.

As shown in Table 4, the reduction of moisture content increases the volume electrical resistance of SBR/CB/PC mortars. With increasing SBR content, the volume electrical resistivity of CBPCA, CBPCb, CBPCc and BPCd are 40500, 9800, 5200, and 4100 ohm.cm respectively. Specifically, for CBPCA, the volume electrical resistivity increases by almost 600%, from 5800 to 40500ohm.cm. For CBPCd, the volume electrical resistivity only increases by 50%, from 2700 to 4100 ohm.cm. For cement matrix composites containing carbon black, the electric conductivity is influenced not only by the number of conductive pathways provided by conductive carbon particles, but also by the transmission of free ions such as $OH^-$, $Na^+$ and $SO_4^{2-}$. Obviously, the reduction of moisture content will decrease the transmission of free ions in the cement matrix, which results in the reduction of electric conductivity.

3.2 Piezoresistivity properties

Results in the literature show that two opposite piezoresistivity behaviors (positive and negative piezoresistivity) can be found in carbon-composites. If the electrical resistivity of the composites increases with increasing pressure, it is called positive piezoresistivity (PP), but decreasing in electrical resistance by increasing pressure is named negative piezoresistivity (NP). The piezoresistivity properties of different cement mortars are given in Table 4 and Figs.3-6. Six specimens for each mix proportion were tested. The results in Table 4 show that under cyclic loading, both PP and NP behaviors can occur in cement mortars. As shown in Table 4, for CBPCa, five specimens showed NP behavior and only one
exhibited PP behavior. However, with the increase of the SBR content, the piezoresistivity tended to be positive. For CBPCd, four specimens showed PP behavior and the other two specimens exhibited NP behavior. Table 4 also indicates that the NP/PP behavior of CBPCA was significantly affected by the variation of moisture content. With the reduction of moisture content, transition from NP to PP behavior was observed. On the other hand, the reduction of moisture had little effect on the piezoresistivity behavior of CBPCd, as most specimens (after first drying or additional drying) showed PP behavior.

Fig. 3 depicts the influence of SBR content on the piezoresistivity value (calculated from eqn(2)) of SBR/CB/PC mortars with higher moisture content (after first drying) in the case of PP behavior. As shown in Fig. 3, the piezoresistivity value increased with the increase of SBR content, with CBPCd having the highest piezoresistivity value of 12.4%, followed by CBPCc with a piezoresistivity value of 8.9%. CBPCA had the lowest piezoresistivity value of 4.4%.

![Figure 3: Piezoresistivities of SBR/CB/PC mortars with PP in 1st test.](image)

Fig. 4 depicts the influence of SBR content on the piezoresistivity value of SBR/CB/PC mortars with lower moisture content (after additional drying) in the case of PP behavior. The piezoresistivity value also increased with the increase of SBR content. Comparing Fig. 4 and
Fig. 3, with the reduction of moisture content, the piezoresistivity value of CBPCa, CBPCb, CBPCc and CBPCd increased by 30%, 25%, 24% and 22% respectively, i.e. the reduction of moisture content of SBR/CB/PC mortars enhanced the piezoresistivity value.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Piezoresistivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SBR 0%</td>
</tr>
<tr>
<td></td>
<td>SBR 5%</td>
</tr>
<tr>
<td></td>
<td>SBR 10%</td>
</tr>
<tr>
<td></td>
<td>SBR 15%</td>
</tr>
</tbody>
</table>

**Figure 4. Piezoresistivities of SBR/CB/PC mortars with PP in 2nd test.**

Fig. 5 presents the influence of SBR content on the piezoresistivity value of SBR/CB/PC mortars with higher moisture content in the case of NP behavior. The magnitude of piezoresistivity values increased with the increase of SBR contents. CBPCd had the highest negative piezoresistivity value of about -10.5%; follow by CBPCc with a value of about -8.4%. CBPCa had the lowest negative piezoresistivity value of about -5.3%.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Piezoresistivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SBR 0%</td>
</tr>
<tr>
<td></td>
<td>SBR 5%</td>
</tr>
<tr>
<td></td>
<td>SBR 10%</td>
</tr>
<tr>
<td></td>
<td>SBR 15%</td>
</tr>
</tbody>
</table>

**Figure 5. Piezoresistivities of SBR/CB/PC mortars with NP in 1st test.**
Fig. 6 presents the influence of SBR content on the piezoresistivity value of SBR/CB/PC mortars with lower moisture content in the case of NP behavior. In this case, the magnitude of piezoresistivity value also increased with the increase of SBR content. Comparing Fig. 6 and Fig. 5, the negative piezoresistivity values of CBPCa, CBPCb, CBPCc and BPCd decreased by 33%, 30%, 25% and 25%, respectively, i.e., the reduction of moisture content of SBR/CB/PC mortars in the case of NP behavior reduced the magnitude of negative piezoresistivity value. This is different from the case of PP behavior in which the reduction of moisture content increased the piezoresistivity value (Figs. 3-4).

![Piezoresistivities of SBR/CB/PC mortars with NP in 2nd test.](image)

**Figure 6. Piezoresistivities of SBR/CB/PC mortars with NP in 2nd test.**

### 3.4 Discussion on modifying mechanism

In existing studies, the electric conductivity and piezoresistivity behavior of CB/PC composites is found to increase with the increase of conductive CB content.\(^1\) Results in this study also show that the increase of insulated SBR content leads to increase in both the electric conductivity and piezoresistivity of SBR/CB/PC composites. This phenomenon can be explained with the help of the schematic illustration in Fig. 7. With increasing SBR content, the amount of agglomerated CB particles decreases while the number of conductive pathways is increased. As shown in Fig. 7a, the geometry dependent clustering occurs when
the host particles (e.g. cement grains) in a composite are much larger and heavier than the
reinforcing materials (e.g. CB). After complete hydration, CB/PC paste consists of hydration
products, void space (gas or fluid filled pore) and CB particles. The CB particles in the fully
hydrated paste will mainly distribute in the regions originally occupied by the mix water in
the fresh state (e.g. CB particles mainly agglomerate in the pores). As a result, few
conductive pathways were formed in CBPCa where only 0.5% of CB (which is far below the
percolation threshold) was incorporated. As demonstrated by SEM (Fig. 2a), apart from the
agglomerated CB particles in the pore (arrows), very few of CB particles could be found in
the fracture surface. When 5 wt.% of SBR content was also added, a lot of pores were sealed
by SBR film (Fig. 7b), thus the amount of agglomerated CB particles was reduced, leading to
an increase in the number of conductive pathways which increases the electric conductivity.
According to existing research studies, when 10 wt.% SBR was incorporated, some
discontinuous polymer networks could be formed in cement composites.\textsuperscript{9-14} It can be inferred
that although the total number of conductive CB particles did not increase in this research, the
number of conductive pathways might increase due to the formation of a new CB-SBR
conductive system, as shown in Fig.7c. For CBPCd with 15 wt.% SBR, a continuous
three-dimensional polymer network was possibly formed throughout the cement mortar (i.e. a
continuous conductive system was formed), leading to a further increase in electric
conductivity, as shown in Table.4.
Results in the literature show that two opposite piezoresistivity behaviors (namely PP and NP) can be found in both cement matrix composites and polymer composites. In addition, the piezoresistivity is influenced by moisture content, range of applied, conductive filler type, structure and volume fraction, etc. The test results observed in the present investigation also indicate the two opposite behaviors, PP and NP, in SBR/CB/PC composites. In order to explain the complicated phenomena leading to such behavior, a new “double effects” model, based on the theory of “tunneling effect” and “capacitance effect”, is developed below.

“Tunneling effect” is based on the theory of quantum tunneling, the tunnel current $I$ of a composite can be calculated by:

$$I = \left(\frac{3e^2U\sqrt{2m\phi}}{2h^2D}\right) \times \exp\left(-\frac{4\pi D\sqrt{2m\phi}}{h}\right)$$

(3)

where $U$, $D$ and $\phi$ are external voltage, the thickness of insulating film and the height of potential barrier, respectively. $h$ is Plank’s constant, $m$ is electron mass and $e$ is electron charge.

Also, the capacitance $C_r$ is obtained from the following equation:

$$C_r = \frac{\pi \varepsilon_r}{\ln(d/a)}$$

(4)
where \( \varepsilon_r \) is the relative dielectric constant between conductor and matrix, \( d \) and \( a \) are the distance and area of the capacitor, respectively.

When an external electric field is applied, electric charges will be oriented along the carbon particles, as schematically illustrated in Fig.8. Between two adjacent CB particles is an insulation layer of hydrated cement hydration or a SBR polymer layer with a high dielectric constant, resulting in the formation of a tiny electric double-layer capacitor. SBR/CB/PC composites, with countless CB particles, possess a great quantity of tiny electric double-layer capacitors which affects the electrical resistance measurements. Because of the very large surface area of the nano-sized CB and very small interval distance among CB particles, electric capacitor made of carbon black has been found to exhibit high power energy storage ability.\(^{21-22}\) Due to the energy storage effect, these capacitors act as traps to increase the resistivity. In this paper, the ability of capacitors to trap electric charge is referred to as “capacitance effect”.

![Figure 8. Schematic diagram of electric double-layer capacitor and the trap effect.](image)

When the compressive loading is continuously varied, both the “tunneling effect” and “capacitance effect” lead to a progressive variation of the electrical resistance in the composite. If the “capacitance effect” plays a dominant role, the electrical resistivity of the
composites increases monotonically upon compressive loading, and piezoresistivity tends to be positive. If the “tunneling effect” plays the main role, the electrical resistivity of the composites decreases monotonically with compressive strain, and piezoresistivity becomes negative. The changing mechanism of piezoresistivity with compressive loading is described as follows. The gap between two adjacent carbon black particles decreases under the increased compression. Based on Eq.3, the smaller gap leads to a smaller $D$, and the resistivity decreases. On the contrary, in Eq.4, the smaller gap leads to a smaller $d$, so the “capacitance effect” with ability of trapping electric charge is increased. The “capacitance effect” of CB composites is stronger than that of “tunneling effect” due to the presence of countless powerful electric double-layer capacitors in the insulating cement matrix. However, if the current intensity is strong enough to break down the capacitance or if the CB particles contact with each other, the “tunneling effect” will play the major role. Therefore, when the content of CB particles is around or above their percolation threshold, the chance for CB particles to come into contact is significantly increased, leading to the negative piezoresistivity (NP), as reported by a number of researchers.\textsuperscript{1-2,5-7}

The influence of SBR on the nature of piezoresistivity (PP or NP) is due to the wrapping up of CB particles by polymer films, which prevents the particles from contacting. As a result, the “capacitance effect” plays the dominant role, and piezoresistivity tends to be positive. Furthermore, the higher the SBR content in CB/PC composite, more CB particles will be wrapped up, so the positive piezoresistivity behavior is more likely to be observed.

The effect of moisture content on the piezoresistivity nature can be explained as follows. For the SBR/CB/PC composite, the electric conductivity is influenced not only by the number of conductive pathways provided by conductive carbon particles, but also by the transmission of free ions such as $OH^-$, $Na^+$ and $SO_4^{2-}$. The transmission of free ions not only leads to an increase of electric conductivity, but also removes the “capacitance effect”. If part or all of
the “capacitance effect” is removed, the piezoresistivity would become negative. The transmission of ions is accelerated with more water, so composites with higher moisture content are more likely to show negative piezoresistivity behavior. For example, CBPCa after the first drying had higher moisture content so the “capacitance effect” was less important. The piezoresistivity behavior was then mainly negative. After additional drying to reduce the moisture content, the “capacitance effect” was enhanced, so the negative piezoresistivity was transformed to a positive behavior. According to Garboczi and Zhao, apart from moisture content, the interconnected pores will also influence the transmission of free ions in cement matrix.\textsuperscript{23-24} The lower the interconnected pore content in cement matrix, the slower is the ions transmission. Both the interconnected pores and the moisture content decrease with the increase of SBR content. Consequently, the transmission of free ions is also decreased. As a result, the addition of SBR decreases the influence of the moisture content on the piezoresistivity.

Test results also show that the reduction of moisture content in SBR/CB/PC composites increased the piezoresistivity value for specimens with PP behavior (Fig.3-4), and decreased the piezoresistivity value (more specifically, the magnitude of the negative value) for specimens with NP behavior (Fig.5-6). This is because the occurrence of PP behavior is attributed to the “capacitance effect”. The reduction of moisture not only decreases the transmission of free ions, but also increases the dielectric constant of cement and polymer in the capacitors. Based on Eqn.4, higher dielectric constant leads to a higher “capacitance effect”. The piezoresistivity value of SBR/CB/PC with PP behavior would therefore increase with the reduction of moisture content. On the contrary, the occurrence of NP behavior is attributed to the “tunneling effect”. The reduction of the moisture decreases the transmission of free ions and increases the height of potential barrier (\(\phi\)). According to Eqn.3, the “tunneling effect” is reduced. For this reason, piezoresistivity of SBR/CB/PC with NP
behavior decreases with the reduction of moisture content.

The deformation ability of cement matrix is also enhanced with the increase of SBR content. As a result, the gaps between carbon particles decrease faster under the same compression loading when more SBR is incorporated. The amplitude of variation in resistivity for cement composites would therefore increase with increasing SBR content. In other words, piezoresistivity is enhanced when more SBR is incorporated.

4. Conclusion

The influence of SBR content on the electric conductivity and piezoresistivity of SBR/CB/PC have been investigated through an experimental research program. Both the electric conductivity and piezoresistivity are found to increase with the increase of SBR content. This enhancement is due to the void-sealing effect of SBR (which prevents the agglomeration of CB particles in voids) as well as its ability to form three-dimensional polymer network, which increases the number of electric pathways. Moreover, the increased deformation ability of cement matrix with increasing SBR content is another reason for the increase in piezoresistivity.

The electric conductivity and piezoresistivity of CB/PC is notably influenced by the moisture content due to its high hydrophilicity and the presence of free ions such as $OH^-$, $Na^+$ and $SO_4^{2-}$. The influence of moisture content on both the electric conductivity and piezoresistivity of SBR/CB/PC is reduced with increasing content of SBR due to its hydrophobic nature and pore-sealing effect.

Two opposite piezoresistivity behaviors, positive and negative, can be found in samples with the same composition. When SBR content is increased and moisture content is reduced, PP behavior becomes more favorable. This phenomenon can be explained by a new “double effects” model based on both the capacitance effect and the theory of tunneling current, which is proposed in this paper.
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