Thermal Stress of Building Materials Containing Rubber Granulate and Polymer Binder Characterised by Alternating Electric Field

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Abstract

The present paper deals with the application of impedance spectroscopy method to test cement-based composites after their exposure to high temperatures. A type CEM I Portland cement, siliceous sand and shredded automobile tires were used to prepare mortar specimens. Various mixtures, different admixture shredded tires and the polymer. The specimens were exposed to high temperatures (temperature range: 23 - 400 °C). Monitoring of structural changes during subjection to thermal stress is an effective way to determine the reliability of specimen structure. Based on Debye’s dielectric theory, the specimens were created dielectric models. Impedance spectra were obtained, while relative permittivity, loss factor and impedance were also measured. The results obtained at each temperature were an indicator of the structural changes and material reliability.

Keywords: Impedance spectroscopy, dielectric losses, loss factor, polymer binder, thermal stress, rubber aggregates, concrete structure

1. Introduction

Cementitious materials are widely used in modern construction. The use of waste tires as such aggregates in polymer modified cementitious materials is an effective approach to massively utilize the waste tire and to avoid its landfill disposal. Concrete and mortars also have some various downfalls. One of these is low toughness which can result in sudden structure collapse. This problem increases with the size and strength of concrete structures. If the yield strength is even locally exceeded it can result in disaster without prior warning. Elevated temperatures multiplies this problem [10-12]. Especially, when the construction is exposed by conflagration. The monitoring of structural changes is very important for determining the reliability of the entire structure. The method that was used for this monitoring is called impedance spectroscopy.

The analysis of changes and description impedance spectra (variances of tan δ (f) and Im Z (f) or Re Z (f)) of inhomogeneous materials is a part of the impedance spectroscopy which is still under development [1,2]. It is not possible to uniquely determine which individual material component contributions to the total electric conductivity and polarization at various frequencies of the alternating field. Thus, we try to evaluate the mortar materials in complex. Materials having higher electric resistance values (over 500 kΩ) can be under certain simplifying assumptions regarded as dielectrics. The theory of dielectric polarization used for homogeneous materials were formulated by Debye’s model. However, experiments carried out with real materials and the respective conclusions did not meet an agreement with Debye’s theory. Therefore, it seems to be mostly appropriate to use the Havriliak-Negami’s model which describes the material behavior comprehensively [3,4]. It is also possible to determine the relaxation time τ or complex values of permittivity ε* (including their components) in this case.

The relaxation polarization [5,6] is a phenomenon characterized by slow response, in contrast to the elastic polarization, in which the recovery is almost instantaneous. The polar particles of different kind, which exist in dielectric material, are only loosely bound to their neighboring ones. These particles will simultaneously perform oscillations and chaotic
displacements with respect to their environment. If an external electric field is applied, thermal movements will be gradually aligned with the direction of this electric field. In this way, there arises a non-symmetric distribution of electric charges, thus giving rise to a dipole moment. Both the polarization growth and decrease (when external electric field is switched off) are proceeding slowly. The relaxation polarization is temperature dependent, being always accompanied by dielectric losses and dielectric heating.

2. Experimental

2.1 Materials

Mortars were produced using a CEM I Portland cement (Českomoravský Cement - Heidelberg Cement Group); aggregates to cement ratio of 2 and water to cement ratio (W/C) of 0.55. Siliceous sand (maximum size of 2 mm) and shredded automobile tires (size in the range of 1 - 2 mm) were used as aggregates.

Acronal S400 (BASF), which is an aqueous anionic dispersion of a copolymer of an acrylic ester and styrene, was used as polymer binder [7,8], (polymer dispersion 20 % w/w of the cement mass).

Another used polymer with trade name Vinnapas 7220 E (Wacker) had material composition of ethylene vinyl(acetate) copolymer (EVA) particles, what is re-dispersible powder in water. Acrylic and EVA copolymers were used as polymer binder (10 % w/w of the cement mass). Each mortar composition and its plasticity are presented in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>Cement [g]</th>
<th>Sand [g]</th>
<th>Rubber aggregates [g]</th>
<th>Polymer binder [g]</th>
<th>Water [g]</th>
<th>Total water [g]</th>
<th>W/C</th>
<th>Plasticity [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG</td>
<td>500</td>
<td>750</td>
<td>250</td>
<td>-</td>
<td>275</td>
<td>275</td>
<td>0.55</td>
<td>13.0</td>
</tr>
<tr>
<td>PAG-AC</td>
<td>750</td>
<td>250</td>
<td>250</td>
<td>100*</td>
<td>225</td>
<td></td>
<td>0.55</td>
<td>15.0</td>
</tr>
<tr>
<td>PAG-EVA</td>
<td>750</td>
<td>250</td>
<td></td>
<td>50**</td>
<td>275</td>
<td></td>
<td>0.55</td>
<td>17.5</td>
</tr>
</tbody>
</table>

* Composition of polymer dispersion Acronal S400 (50 g water + 50 g acrylic polymer)
** Polymer powder Vinnapas 7220 E does not contains water

The use of waste tires as concrete aggregate is an economical disposal solution. Many research results indicate that the presence of rubber aggregates can not only obviously improve the ductility and toughness of concrete but also overcome the weakness of concrete’s brittleness [15]. The use of polymer–rubber aggregate modified porous concrete is an effective approach to massively utilize the waste tire.

In this paper, the scrap tires rubber aggregate is used as substitute for the mineral aggregate of the polymer modified porous concrete to improve the flexibility and ductility of the pavement friction course. Hence a new type of polymer–rubber aggregate modified porous concrete friction course is prepared, and the mechanical properties, abrasion and impact resistance and the porosity of this material are investigated. The morphology of hydration products and the microstructure of the interfacial transition zone are observed with SEM [14,15].

Mortar specimens (prisms: 40 mm×40 mm×160 mm) were prepared. The specimens were left in the moulds for 24 hours, then cured in water for 27 days and finally air-cured for 32 days at laboratory temperature (25±2 °C).
2.2 Tests

The mortar specimens prepared were characterized by applying the impedance spectroscopy method. Sinusoidal signal generator Agilent 33220A and oscilloscope Agilent 54645A were used. These devices were set according to the diagram suggested by [5]. In order to perform impedance analysis, samples were mounted between brass electrodes with a surface of 7 x 3.5 cm. Specimens were measured in frequency spectra range between 40 Hz till 1 MHz. The spectra of loss factor tan δ (f) versus frequency were obtained, as well as the dependences of the imaginary part Im Z (f) and the real part Re Z (f) on frequency. The capacitance C was calculated for each frequency.

3. Results and discussion

The beginning of the work introduces the comparison and dependence of loss factor (tan δ) at a frequency (f) for the reference specimen (PAG) with rubber aggregates and without plasticizer (binder). These results are shown in Fig.1. Specimen displayed important change in the mortar structure; 25 % of silicone sand are replaced by rubber aggregates. The observed frequency range was also from 40 Hz to 1 MHz. In this case, un-annealed sample (stored at 23 °C) reached a loss factor (tan δ) between 0.3 - 0.6. The exposure of PAG specimen in temperature 200 °C resulted in extreme increasing of (tan δ) values up to 1.0, in the whole applied frequency range of 40 Hz to 1 kHz. Declining of the curve, which also describes a loss of the polarization, is mostly visible in frequencies 10^3 - 10^6 Hz. The influence of lost conductivity is dominant in this case. The phenomenon was caused by the presence of rubber which probably created better connections with mortar components during the heat stress. The following temperature elevation to 300 °C and 400 °C started thermo-oxidative rubber degradation. The generated degradation products provided physical connection between particles of the mortar and the rubber. The result was increased surface conductivity of rubber particles. It causes extreme reduction of loss factor (tan δ) until value 0.2 at wide area of measured frequencies. Values of (tan δ) in higher frequencies were as low as limit of measurability was.

Fig.2 describes the change of relative permittivity (ε_r), the real part impedance (Re Z), the imaginary part of impedance (Im Z) and the absolute value of the impedance |Z| of specimen PAG during a heat stress 23 °C to 400 °C. The chosen reference frequency of excitation electric field was 1 kHz. Relative permittivity (ε_r) of PAG samples stored at 23 °C had a value of 185. When the exposition temperature was elevated (ε_r) decreased in values: 59 at 200 °C, 25 at 300 °C and only 22 at 400 °C. The relative permittivity of samples exposed above 300 °C showed irreversible changes in the structure of the rubber again. Values of the real part impedance (Re Z), imaginary component of the impedance (Im Z) and absolute impedance value |Z| increased with elevated exposing temperature. All these values are also very close above 300 °C.

The impedance |Z| of specimen PAG (including its components) was ranged from 0.3*10^6 Ω to 1.4*10^6 Ω before it was annealed. The exposing at 200 °C resulted in increasing of these values close to order of magnitude. The exposing to 300 °C continued in (Im Z) and |Z| increase. Therefore, it is supposed that in PAG specimens exposed above 300 °C occurred carbonizing of rubber aggregates as was mentioned above. Following conductivity increasing fulfills the behavior of thermal decomposition of SBR rubber when the generation of polar substituents was observed [16-18]. All obtained values are placed in Table 2.

As the mortar were heated the following changes gradually took place. The capillary water was evaporated and cohesive forces were reduced due to expansion of moisture up to 80 °C. The Ettringite dehydrate at temperatures of 80 - 150 °C and the gypsum is decomposed
around temperature 170 °C according to \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \). This resulted in explosive spalling. Temperatures above 200 °C led to loosing of physically bounded water and increasing of internal pressure inside the specimen and temperatures about 350 °C resulted in cracking of silica aggregates. With temperature above 375 °C water was not present. The decomposition of Portlandite should be observable above 400 °C (\( \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \)) [9-12].

The dependence of the loss factor \((\tan \delta)\) at frequency \((f)\) for specimen PAG-AC is observable in Fig.3. The specimens has the same composition as PAG, however, acrylic polymeric binder Acronal S400 was added in 10 % (w/w) of amount of cement mass. The observed frequency range was again 40 Hz - 1 MHz. Various curves correspond to different thermal stresses. The almost similar loss factor \((\tan \delta)\) is observable in spectra of specimens PAG and PAG-AC (Fig.1 and Fig.3) stored at 23 °C. The deviation occurred when the frequency was > 10^5 Hz. Significant difference was found for samples exposed above 200 °C, wherein the decrease occurred in the whole frequency spectrum. Sample with a plasticizer did not show any increase at 200 °C. The reduction of polarization loss was observable in case of PAG, however this phenomenon was not present when AC binder was added. Nevertheless, decrease of loss factor \((\tan \delta)\) was recorded above 300 °C - it was mentioned in hypothesis of rubber thermal degradation.

As similar as Fig.2, the Fig.4 also describes the change of \((\varepsilon_r)\), \((\Re Z)\), \((\Im Z)\) and \(|Z|\) during a heat stress 23 - 400 °C, however of specimen PAG-AC. The chosen reference frequency of excitation electric field was also 1 kHz. Relative permittivity \((\varepsilon_r)\) of PAG samples stored at 23 °C had a value of 121. When the exposition temperature was elevated \((\varepsilon_r)\) decreased in values: 38 at 200 °C 19 at 300 °C and only 16 at 400 °C. In summary, behavior of all electrical characteristics \((\varepsilon_r)\), \((\Re Z)\), \((\Im Z)\) and \(|Z|\) of the specimen PAG-AC exposed above 300 °C were similar to specimen PAG. Moreover, the thermal decomposition of SBR rubber aggregates was also observed above 300 °C which were followed by conductivity increase. The impedance \(|Z|\) of specimen PAG-AC and its components were also in the same trend as results of specimen PAG was. Values \((\Re Z)\), \((\Im Z)\) and \(|Z|\) were increased with elevated heat stress. Rubber aggregates were decomposed above 300 °C and extreme reduction of impedance values followed. Values of impedance \(|Z|\) (without specifying the component of the impedance) were placed between 1.0*10^6 Ω to 2.2*10^6 Ω before it was annealed. The exposing at 200 °C achieved increasing of these values to be between 3.2*10^6 Ω to 6.9*10^6 Ω. Values continued by exposing at higher temperature in 15.5*10^6 Ω (300 °C), resp. 19.1*10^6 Ω (400 °C). All obtained values are summarized in Table 2. Values of the impedance of
specimen PAG-AC were higher than values of specimen PAG. On the other hand, the electrical capacity of the sample mixture PAG-AC was lower.

The addition of polymer binder was a component with a different polarity than the cement, sand and water were. Heating the polymer leads to a gradual thermal degradation. In case of acrylic binder Acronal, the decomposition started by rupturing of functional groups and continued by the elimination of water and carbon dioxide (approx. 150-300 °C). It resulted in cycling of polymer chains which are unstable at higher temperatures. The acrylic polymer lost its mechanical properties (strength and flexibility). The next step was the thermal degradation at temperature of 300-400 °C. It graduated in tearing of the polymer chains, double bonds formation and generation of free radicals [13,14]. These degradation steps achieved in subsequent carbonization and losing of the polarity of the polymer, its conductivity and permittivity also.

Fig. 3 Loss factor on depended on frequency diagram (PAG-AC)

Fig. 4 Relative permittivity and components of impedance (PAG-AC, f = 1 kHz)

Fig.5 describes the dependence of the loss factor (tan δ) at a frequency (f) for specimen PAG-EVA. The specimens have the same composition as PAG, however, redispersible powder of EVA polymer was added in 10 % (w/w) of amount of cement. Tested frequency range was 40 Hz - 1 MHz. Results from Fig.3 and Fig.5 were compared. The almost similar loss factor (tan δ) was observable in case of specimens exposed by all elevated temperatures 200, 300 and 400 °C. Characteristic curves, however, are very similar. The deviation in whole frequency range was recorded only before heating stress (at 23 °C). The rubber thermal degradation above 300 °C was also observed.

Fig.6 describes the dependence of electrical characteristics of the specimen PAG-EVA. Relative permittivity (εr) and all compounds of impedance (Re Z), (Im Z) and |Z| are displayed. The reference frequency of excitation electric field was also 1 kHz. The figure compare obtained values on degree of applied heat stress 23 - 400 °C. The relative permittivity (εr) stored samples at 23 °C had a value of 78. When the exposition temperature was elevated (εr) decreased in values: 26 at 200 °C 18 at 300 °C and only 15 at 400 °C. Discrete values of relative permittivity (εr) at 300 °C and 400 °C were very similar in comparison to used acrylic binder (see Fig.4). Its values for exposing temperature were decreased about 1 unit. Values of relative permittivity (εr) of specimen PAG/EVA were about 5-36 % lower than the PAG-AC, for all annealing temperatures (compare Fig.4 and Fig.6).

The impedance |Z|(including its components) had similar behavior for specimen PAG-EVA as specimen PAG had. Values were placed between 1.7*10^6 Ω to 3.2*10^6 Ω before annealing of the specimen. The exposing at 200 °C achieved increasing of these values between 3.8*10^6 Ω to 13.9*10^6 Ω. Values continued by exposing at higher temperature in 16.4*10^6 Ω (300 °C), resp. 19.3*10^6 Ω (400 °C).
The behavior of all electrical characteristics (Re Z), (Im Z) and |Z| of the specimen PAG-EVA exposed above 300 °C were as similar as specimen PAG was. It confirmed previous summary that the major changes in modified mortar structure were achieved by the thermal decomposition of used rubber aggregates. This trend was mostly observable when PAG, PAG-AC and PAG-EVA specimens were exposed above 300 °C which followed increased conductivity.

In total, behavior of all electrical characteristics (Re Z), (Im Z) and |Z| of the specimen PAG-EVA was placed in higher values than the specimens PAG and PAG-AC were. Although, values of real part of impedance (Re Z) were after heat stress above 200 °C relatively close to specimen PAG-AC. Values (Re Z) and (Im Z) had the same increasing trend. All obtained values are summarized in Table 2. There is possible to see that impedance values of PAG-EVA are higher that values of PAG-AC were. On the other hand, the electric capacitance of PAG-EVA is lower in this case.

### Table 2. Electrical parameters of specimens, measured with reference frequency of 1 kHz

| PAG-AC / PAG-EVA | ε_r [-] | Re(Z) [MΩ] | Im(Z) [MΩ] | |Z| [MΩ] | C [pF] |
|------------------|----------|-------------|-------------|----------|--------|
| 23 °C            | 185      | 0.68        | 1.22        | 1.39     | 100.38 |
|                  | 121/78   | 1.04/1.74   | 1.86/2.61   | 2.13/3.14| 65.63/42.51 |
|                  | 59       | 2.40        | 3.29        | 4.08     | 31.80 |
| 200 °C           | 38/26    | 3.21/3.88   | 6.07/10.07  | 6.87/10.79| 20.64/13.88 |
|                  | 25       | 2.14        | 11.22       | 11.43    | 13.78 |
| 300 °C           | 19/18    | 2.26/1.99   | 15.31/16.18 | 15.48/16.31| 10.25/9.63 |
|                  | 22       | 1.85        | 12.92       | 13.05    | 12.17 |
| 400 °C           | 16/15    | 2.94/2.57   | 19.04/19.04 | 18.66/19.21| 8.49/8.28 |

4. Summary

The paper described the change of the electrical parameters of cement mortar specimens made with sand and waste tires as aggregates and incorporating or not acrylic/EVA polymer binder addition. The specimens were also subjected to thermal stress and their structure changes were observed in regard to alterations of relative permittivity, loss factor and impedance values. The impedance spectra values of the two kind of specimens were calculated and
differences were observed. The gradual degradation of the acrylic polymer resulted in
cleavage of the functional groups and subsequent carbonization. Thus, it lost polarity, its
cconductivity and permittivity.

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