MATERIALE COMPOZITE LIANTE CU CONŢINUT DE TITANAT DE BARIU PENTRU OBȚINEREA UNOR STRUCTURI INTELIGENTE
CEMENTITIOUS COMPOSITES CONTAINING BARIUM TITANATE FOR OBTAINING OF SOME SMART STRUCTURES

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This study presents the obtaining and characterization of some special mortars intended for smart constructions, having in composition Portland cement (PC) with addition of barium titanate nanopowder (BTNp). A main characteristic of these cementitious composites is piezoresistive behavior. These materials, based on PC with BTNp, can identify the stress within as a variation of electrical resistance; therefore, this type of cementitious composites (mortars and concrete) could have an important role in monitoring infrastructures as a nondestructive method. The BTNp was obtained by a combination of sol-gel and hydrothermal methods starting form tetrabutyl titanate and barium acetate. The mortars based on PC and BTNp were characterized from the point of view of specific properties (electrical resistance, mechanical strengths). Variation of electrical signal when applying a mechanical strain was the main specific property studied in terms of self-sensing materials.

The compositional and microstructural characteristics of mortars strongly influences the mechanical strength values and electrical signal. The compressive and flexural strength values were assessed on hardened mortars for 28 and 90 days; those of mortars containing barium titanate, are comparable with the ones of the mortar without BTNp. The values of electrical resistance are strongly correlated with the composition, morphology, and hardening time of mortars. The experimental results presented in this study demonstrate that BTNp addition can reduce the electrical resistance of cement-based matrices. Regardless of the hardening time, in all mortars, one can observe that the presence of BTNp does not change the nature of specific phases formed by hydration of Portland cement and does not lead to the formation of other new hydration phases.

Acest articol prezintă obţinerea şi caracterizarea unor mortare speciale destinate pentru construcții inteligente, utilizând în compoziție ciment Portland (PC) cu adaos de nanopulbere de titanat de bariu (BTNp). O caracteristică principală a acestor compozite liante este comportamentul piezorezistiv. Materialele liante anorganice pe bază de PC și BTNp prezintă proprietăți piezorezistive. Cu ajutorul unor astfel de compozite, care acționează ca un senzor, se poate monitoriza rezistența electrică a materialului și implicit rezistența în timp a infrastructurii, ca și metodă nedistructivă. Nanopulberea de titanat de bariu utilizată a fost sintetizată în laborator utilizând metoda combinată sol-gel și hidrotermal având drept constituenţi de bază butoxid de titan şi acetat de bariu. Mortarele pe bază de PC cu adaos de BTNp au fost caracterizate din punct de vedere al proprietăţilor specifice (rezistența electrică, caracteristici mecanice), iar variaţia semnalului electric cu aplicarea unei forţe este principala caracteristică a acestor materiale liante cu destinaţii speciale.

Caracteristicile compoziționale și microstructurale ale mortarelor influențează puternic semnalul electric și valorile rezistenței mecanice. Rezistențele mecanice atât la compresiune cât și la încovoiere, au fost analizate la 28 şi 90 de zile; valorile obținute în cazul mortarelor cu conținut de BTNp sunt similare cu cele fără titanat de bariu. Valorile rezistenţei electrice sunt corelate cu morfologia, compoziția precum și perioada de întărire a probelor obţinute. Din datele experimentale obținute se poate observa că adiția de BTNp în matricele liante pe bază de ciment Portland, scade rezistența electrică a acesteia. La toate perioadele de întărire se poate observa că prezența BTNp nu modifică natura fazelor de hidratare specifice hidratării cimentului Portland și nici formarea altora noi.

***Keywords**: Portland cement, barium titanate, electrical properties, special mortars*

1. Introduction

The degradation of civil infrastructures due to load, fatigue, erosion, or aging is the main reason for failure of concrete structures. In modern construction industry a critical aspect is related to monitoring civil infrastructures and, as a result, today, SHM (structural health monitoring) is a key component of infrastructures monitoring. This new discipline's purpose is to extend the life service of buildings and provide information regarding durability. Usually, sensors used for SHM are made of metals; due to the fact that they are usually attached to concrete, they can easily be corroded or/and separated and thus they do not serve their initial purpose [1]. Also, an important part in the maintenance of concrete structures is represented by structural health monitoring in today world. As a result, the need of using sensors to monitor the structural behavior becomes necessary. Structural characteristics of composite materials such as mortars and concrete can be monitored, in a non-destructive way, by using piezorezistivity. Recently, there has been a development in obtaining cement-based sensors embeddable in structures able to measure the change in resistivity [2,3].

Cementitious materials have a certain electrical resistivity that can be reduced by adding various conductive fillers. Piezoresistivity is a physical property of materials and is defined as

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change of the electrical resistivity when a material is subjected to mechanical strain [4].

There are three microscopic phases present in a cement-based sensor: cementitious matrix, wich containing the hardening phases and evoluating in time; aggregates and eventual anhydrous cement; piezoresistive fillers. An important role concerning mechanical and electrical behavior is played by the interfaces between these phases. The highest effect on the electrical conductivity is given by the interfaces between filler particles [5]. Nano- or micro-scale fillers are usually used because of their higher potential for connecting to one another. Various types of fillers i.e. carbon nanotubes [1, 6], carbon fibres [7,8], barium titanate [9-12], carbon black [13,14], steel fibers [15] and nickel powder [16] were used up to now to obtain cement based sensors.

Cementitious composites containing barium titanate presents piezoresistive behavior [17]. These materials, based on PC with BTNp, can identify the stress within as a variation of electrical resistance; as a result this type of cementitious composites (mortars and concrete) could have an important role in monitoring infrastructures as a nondestructive method [9-12, 17]. A main condition of these new materials is that nanofiller addition should not affect concrete's main properties (as construction material).

For reaching the main objective of this research (self-sensing cementitious mortars with adequate construction properties) barium titanate was selected as nanofiller because of its good dielectric properties, high thermochemical stability. BT was obtained, by a combination of sol-gel and hydrothermal methods, starting form tetrabutyl titanate and barium acetate.

Impedance spectroscopy (IS) is a widely tool used to assess the changes in the electrical properties of mortars subjected to mechanical stress in a non-destructive manner [18-20].

2. Materials and methods

2.1 Materials

Portland cement (PC) CEM I 42.5R and a barium titanate nanopowder were used as raw materials. The oxide composition of PC (63.78 % CaO, 20.12%SiO_2, 4.58% Al_2O_3, 3.99% Fe_2O_3, 1.20% MgO, 2.61% SO_3 and 3.72% LOI) was assessed by chemical method presented in EN 196-2:2013 [21]. BT was obtained by a combination of sol-gel and hydrothermal methods, starting form tetrabutyl titanate and barium acetate similar with [22] (hydrothermal conditions: 120°C, 24 h; 4 M KOH).

Two types of specimens were prepared:

- mortars, with water to binder ratio of 0.5 and cement to aggregate ratio of 0.33; the aggregate was natural sand as specified in European norm EN 196–1, part 1 [23]. In order to assess the influence of barium titanate nanopowder additions on the compressive strengths and electrical properties, the mortars were cast in rectangular moulds (40x40x160mm), then were vibrated for 2 minutes and hardened for 28 and 90 days in humid air (R.H. 90%);
- cement pastes with/without BT addition, having a water to binder ratio of 0.5.

By vigorous magnetic stirring the barium titanate nanopowder was dispersed in water and then was mixed with the other components (PC and sand - in the case of mortars). PC was substituted by various amount of BT powder: 5% (BT5) and 15% (BT15). The sample without BT, with 100% PC was considered the etalon sample (E).

2.2. Methods

Using a Shimadzu XRD 6000 diffractometer, the mineralogical composition of PC and BT were assessed (Ni-filtered CuKα radiation - α=1.5406 Å; 2 theta in 5-80° range). Also, by using a QUANTA INSPECT F scanning electron microscope (SEM) the morphology of BT powder and the microstructure of hardened mortars for 28 and 90 days were assessed (the limits of the microscope were 1.2 nm resolution at 30 kV and 3 nm at 1 kV for BSE; the samples were coated with gold).

The requirements of European and corresponding Romanian norm SR EN 196-3 [24] were followed when evaluating setting time of cement pastes and water for normal consistency.

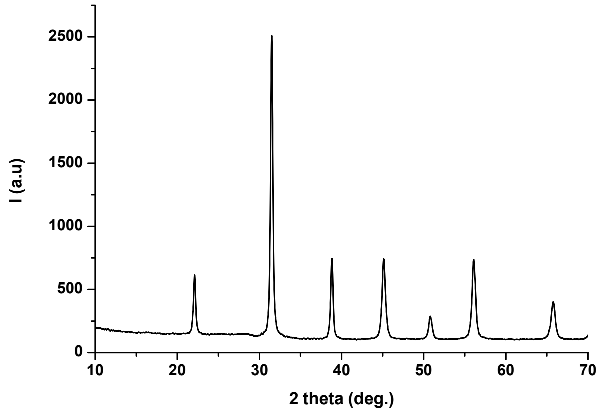
In accordance with the method presented in EN 196–1:2016 [23] and using a Matest machine flexural and compressive strength were assessed; the given values represent the average of least four values assessed on mortar specimens hardened similarly.

Using a SI 1260 Impedance Analyzer, the specimens were tested by alternating current (AC) impedance. The experimental set-up was as previously reported [25], been the measurements were performed using an arrangement of two electrodes (l x L x h=20 x 30 x 3 mm at distance 40 mm).

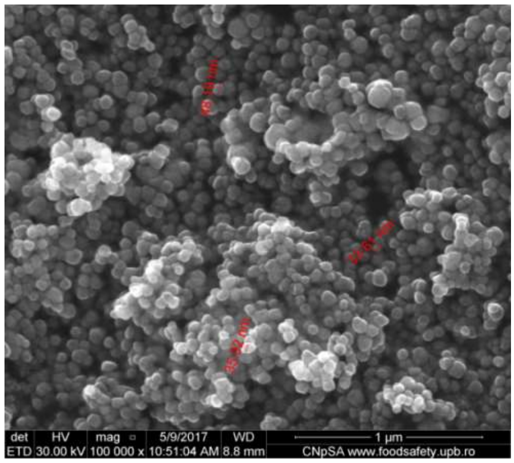
Measurement of impedance without load for 7 minutes was the first step, after that followed of loading protocol. Impedance measurements were performed from 5 MHz down to 1Hz at an amplitude of the sinusoidal voltage equal to 1.5 mV. The procedure was incrementally repeated until the sample was broken, for higher pressures.

3. Results and discussions

Using XRD, the mineralogical composition of PC, was assessed; the X-ray diffraction pattern presented specific peaks for the main mineralogical compounds of Portland clinker: calcium aluminate ($Ca_3Al_2O_6$; JCPDS 33-0251), belite (Ca_2SiO_4; JCPDS 33-0303) and alite (Ca_3SiO_5; JCPDS 42-0551).



a



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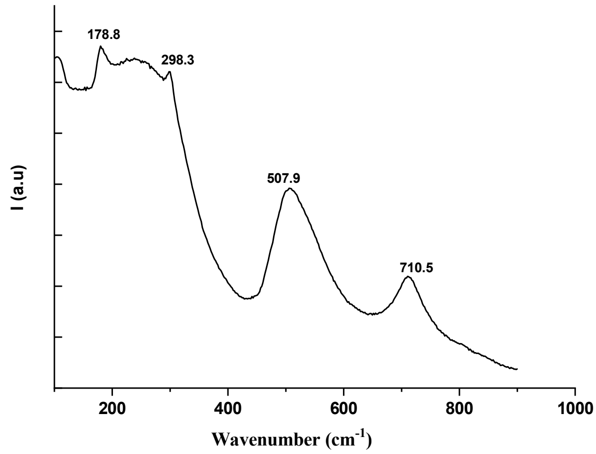
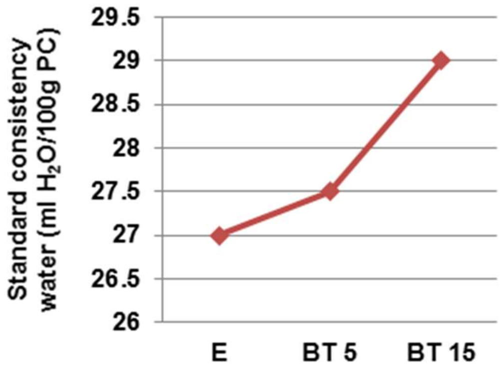


c

Fig. 1 - XRD pattern (a), SEM image (b) and RAMAN spectra (c) of BT nanopowder / *Difracția de raze X (DRX) (a), imaginea de microscopie electonică de baleiaj (MEB) (b) și spectrul RAMAN (c) pentru nanopulberea de BT* .



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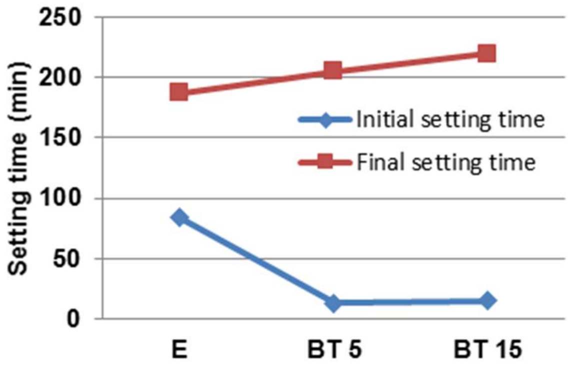
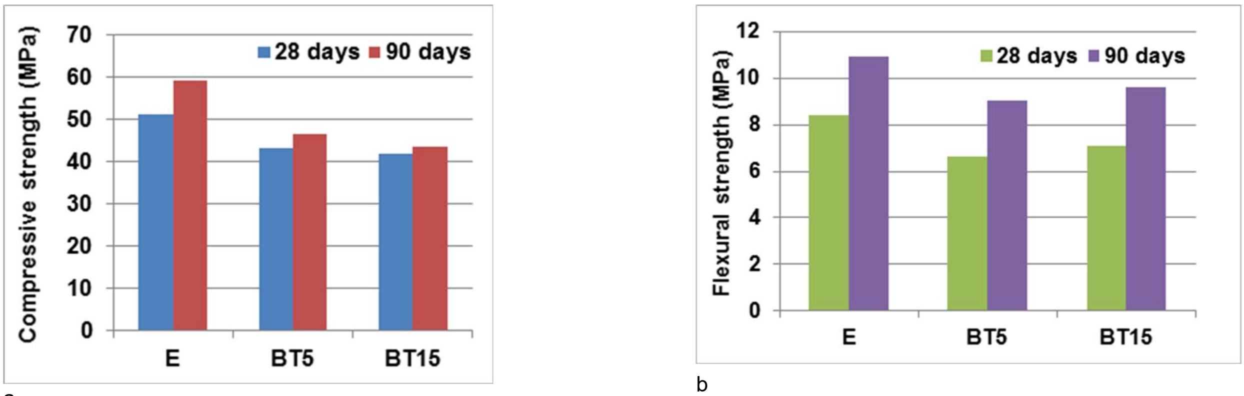


b

Fig. 2 – Water for standard consistency (a) and setting time (b) for E, BT5 and BT15 / *Valorile apei de consistenţă normală (a) şi timpii de priză (b) pentru E, BT5 şi BT15.*

As shown in Figure 1a, XRD pattern confirms the presence of barium titanate, in cubic form, according to JCPDS 079-2263. The microstructure of BT nanopowder is presented in fig. 1b and reveals the presence of very small particle (smaller than 50 nm) with polyhedral morphology; one can notice their tendency to agglomerate as aggregates. In contrary to the XRD analysis, the recorded Raman spectra (Figure 1 c) showed a pseudo-cubic or tetragonal symmetry, by the presence of the bands at 179, 298, 508 and 711 cm^{-1}. This is explained by a slight distortion of tetragonal $BaTiO_3$ lattice and the BTNp can have a piezoresistive character.

The variation of the amount of water for normal consistency as a condition of partial replacement of PC with various amounts of BTNp is presented in Figure 2. The amount of water for normal consistency varies dependently with BT dosage; this is due to the fact that BTNp has a high water adsorption capacity. Initial setting time of samples containing BT (5% and 15%) has significantly smaller values compared with portland cement (E). Compared with PC (E), final setting



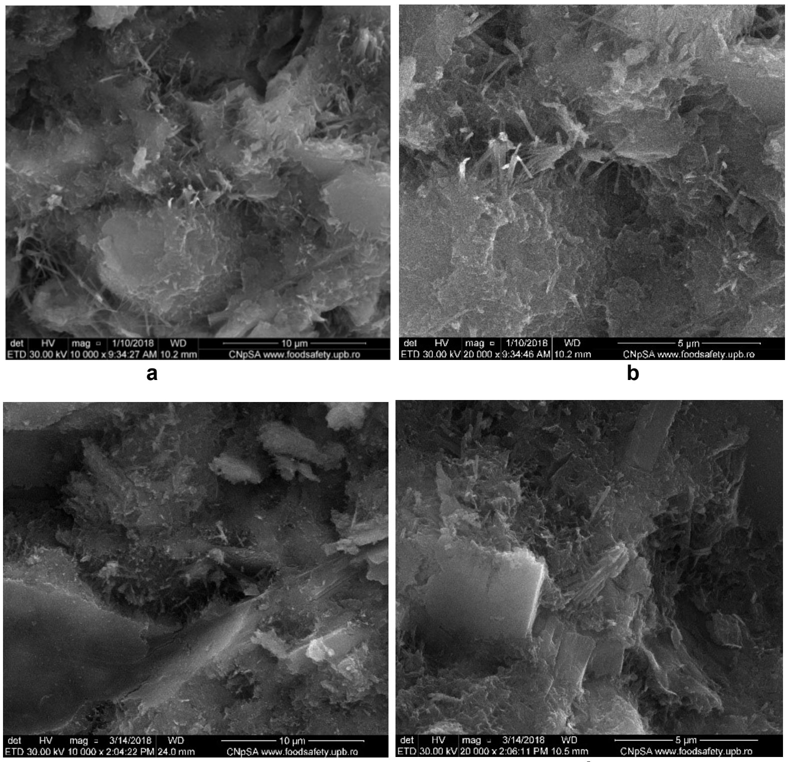
a b

Fig. 3 - Mechanical strength variation dependent on BT amount: a - compressive strength, b - flexural strength
Variaţia rezistenţei mecanice funcţie de cantitatea de liant substituită: a - rezistenţa la compresiune , b – rezistenţa la încovoiere.

time of BT5 and BT15 is bigger; one of the reasons for this is the release of an amount of water, initially absorbed on barium titanate particles, in the system.

In Figure 3 are presented the evolution with hardening time of compressive and flexural strengths. Flexural as well as compressive strength has increased values with regards to the evolution in time. Hardening processes and the development of PC hydration is the main reasons for this. One can notice a small decrease of both compressive (20%) and flexural (12%) strengths with the substitution of Portland cement with different amounts of BT determines. The increase of BT amount (from 5% to 15%) have a small influence on the strength values of mortars.

Figures 4 and 5 presents the microstructure, assessed by SEM, of mortar specimens with/without 15 wt.% BT, hardened for 28 and 90 days respectively. Regardless of hardening time, for all studied mortars, it can be observed the presence of aggregate and specific phases: portlandite ($Ca(OH)_2$) - hexagonal plates; ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$; AFt) - needle-shaped formations; monosulphate phase (AFm) and calcium carbonate - parallel planes particles; gypsum - prismatic crystals; calcium silicate hydrates (CSH) - fine needles and films. For longer hardening times (90 days), one can also observe an increase of hydrates sizes and a densification of cement stone.



c d

Fig. 4 – Scanning electron microscopy images for E hardened for 28 days (a, b) and 90 days (c, d)
Fig. 4 – Imagini SEM pentru proba etalon întărită 28 de zile (a, b) şi 90 de zile (c, d)

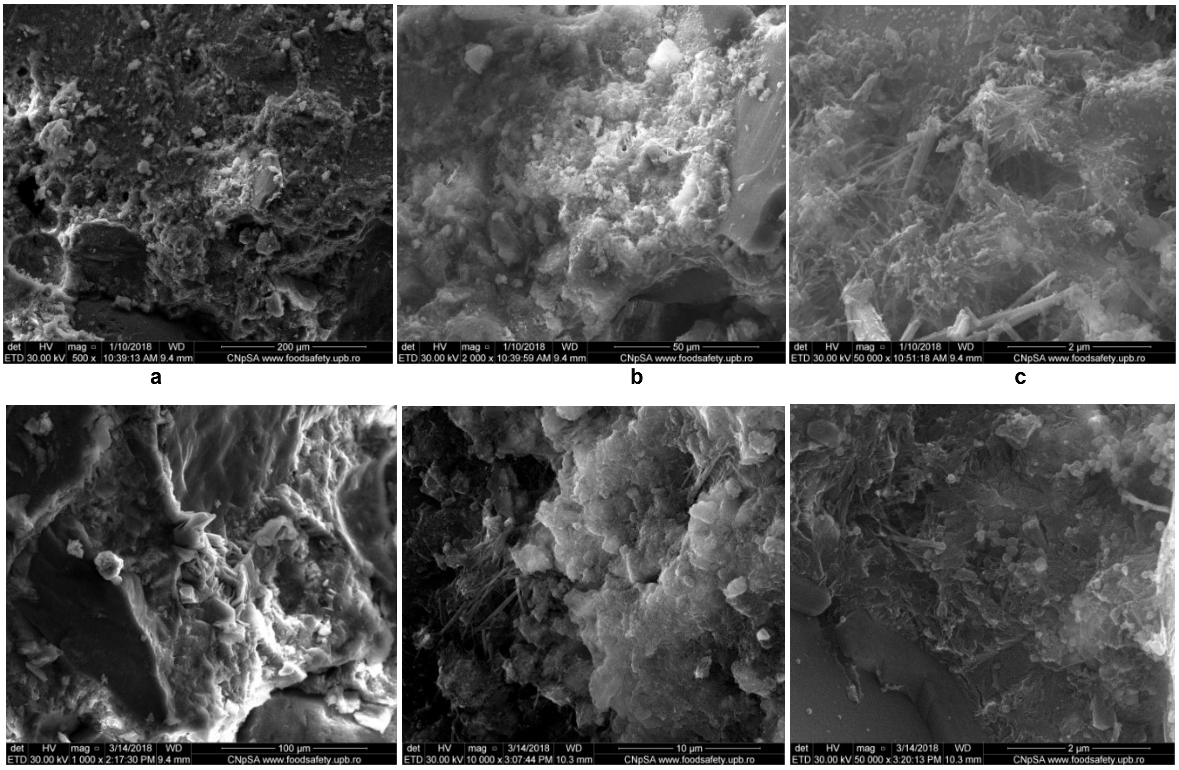


Fig. 5 – Scanning electron microscopy images for BT15 hardened for 28 days (a, b, c) and 90 days (d, e, f).
Imagini SEM pentru proba BT15 întărită 28 de zile (a, b, c) şi 90 de zile (d, e, f).

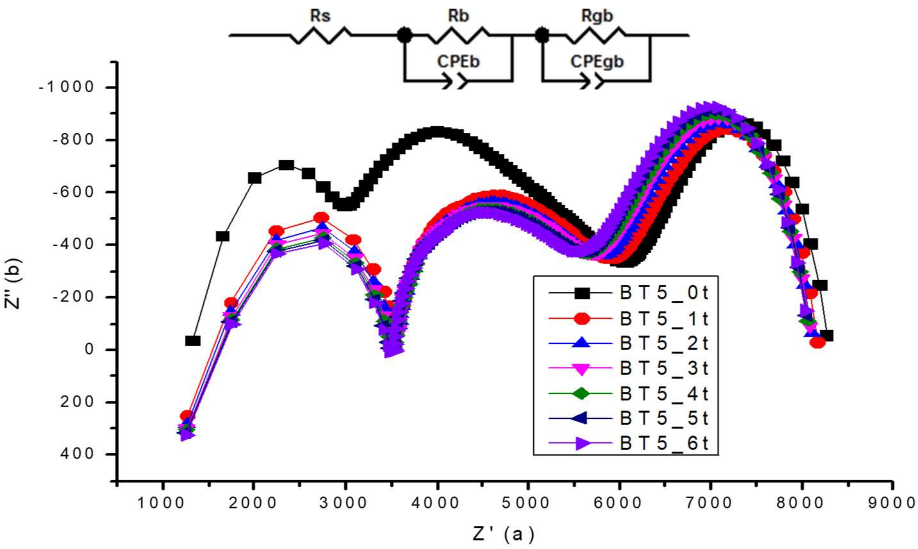


Fig. 6 – Impedance plot for BT5 hardened for 28 days with different loading effort and equivalent circuit (detail above).
Impedanţa mortarelor cu 5% BT întărite 90 de zile la variaţia efortului de încărcare și circuitul echivalent (detaliu sus).

AC measurement results can are provided as the Nyquist plots and are specific piezoresistivity tests. On hardened mortars for 90 days, were performed specific piezoresistivity by the AC measurements. The loads were applied, (see cap. 2.2), in the longitudinal direction of specimens, on the two ends of the mortar specimens. The following equation is used to calculate the piezoresistivity of each mortar specimen [25]:

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \times 100\% \quad (1)$$

where R - resistance; R_0 initial value (prior to any loading).

AC electrochemical impedance spectroscopy results in this study have the same trend and thus, the variation for BT5 at different loadings is presented in Figure 6. This plot is composed by a semicircle which corresponds to different electrical resistances (interior grain-Rg, grain boundary-Rgb) as well as the contribution of electrodes; also, can see to the conventional equivalent circuit which fits this type of impedance plots.

It is formed by constant phase elements (CPE) and a series of two sub-circuits of parallel resistors (R). The non-ideal behavior of the capacitance is due to the presence of more than one relaxation process with similar relaxation times. CPEg is the constant phase element for grain interior and CPEgb represents the constant phase element for grain boundaries.

For all studied compositions, electrical resistivity increases continuously. The morphological and structural modification taking place in these materials can explained this fact. Tortuosity, porosity of the pore network, the composition and amount of pore solution are the main factories that influence the electrical resistivity of concrete [26]. Electrical properties of the material (the increase of the crystallinity of formed hydrates, strain-stress effect, the evaporation of water from the system, shrinkage) can be modified by the changes of these parameters. An important impact on the Rg and Rgb values is represented, especially at longer hardening period of time, by the increase of size and crystallinity degree of hydrates formed during the cement hydration. The electrical resistance of the obtained materials can be significantly reduced by increasing the amount of BT used – Figure 7. BTNp is localized in intergranular area and thus mortars containing this nanopowder have a higher response to electrical stimulus.

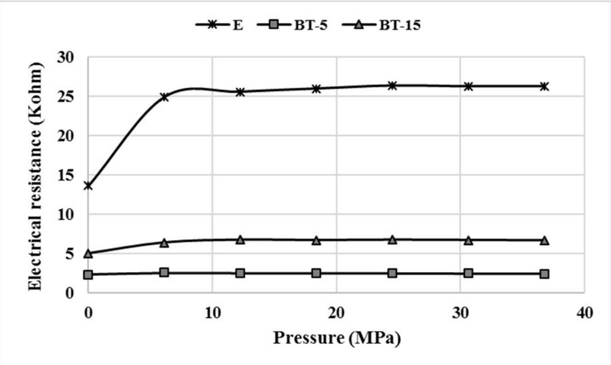


Fig. 7 – The electrical resistance (Rg+Rgb) values for E, BT5 and BT15 hardened for 90 days with different loading pressure / *Rezistența electrică pentru masele E, BT5 și BT15 întărite 90 de zile la variaţia presiunii de încărcare*.

Conclusion

This study demonstrates the fact that BTNp addition can reduce the electrical resistance of cement-based matrices. The addition of BT (up to 15wt.%) in mortar formulation determines some small strength losses as a result of the decrease of mechanical properties. Regardless of hardening time and addition of BTNp, in all mortars, it was demonstrated that Portland cement hydration process lead to the presence of hydrated phases, as expected.

Intergranular electrical resistance (Rgb) on the electrical behavior of the investigated samples have a major influence and it was demonstrated by AC electrochemical impedance spectroscopy (EIS) observations. Composition, morphology, and hardening time of the mortars are strongly correlated with the values of electrical resistance. As a result, monitoring the change of electrical resistance of mortars with barium titanate substitutions, can give essential information regarding damage degree in contemporary smart structures.

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