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POLIMERY

Effect of batched water exposed to a constant magnetic field on the properties of concrete filled with waste fly ash, phosphogypsum and starch

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Abstract: The influence of batched water exposed to a constant magnetic field (B = 1 T) on the properties of concrete was investigated. Fillers such as coal fly ash (CFA), phosphogypsum (PB) and native potato starch dispersed in epoxy resin [EP(S)], were used to obtain concrete based on Portland cement (PC). The magnetized batched water had a positive effect on the properties of concrete, reducing water absorption and increasing flexural and compressive strengths. The obtained concrete is a new promising building material that can be used to manufacture e.g. building foundations, flush-mounted installations and insulation layers.

Keywords: coal fly ash, phosphogypsum, native starch, concrete.

Wpływ wody zarobowej poddanej działaniu stałego pola magnetycznego na właściwości betonu wypełnionego odpadowym popiołem lotnym, fosfogipsem i skrobią

Streszczenie: Zbadano wpływ wody zarobowej poddanej działaniu stałego pola magnetycznego (B = 1 T) na właściwości betonu. Do wytwarzania betonu na bazie cementu Portlandzkiego (PC) użyto napełniaczy takich jak popiół lotny ze spalania węgla (CFA), fosfogips (PB) i natywna skrobia ziemniaczana zdyspergowana w żywicy epoksydowej [EP(S)]. Zastosowanie namagnetyzowanej wody zarobowej wpłynęło korzystnie na właściwości betonu zmniejszając jego nasiąkliwość oraz zwiększając wytrzymałość na zginanie i ściskanie. Otrzymany beton jest nowym, obiecującym materiałem budowlanym z którego można wytwarzać np. fundamenty budynków, instalacje podtynkowe i warstwy izolacyjne.

Słowa kluczowe: popiół lotny ze spalania węgla, fosfogips, skrobia natywna, beton.

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Coal fly ash (CFA) is a solid waste product of the burning of pulverized coal in coal-fired power plants and it contains metal oxides such as SiO_2, Al_2O_3, and Fe_2O_3, unburnt carbon, and radioactive isotopes of thorium, uranium and potassium [1, 2]. CFA can be captured and collected from the flue gases using particle filtration devices such as electrostatic precipitators and cyclones. The most important application of waste CFA is the production of Portland cement clinker, cements, concrete, light aggregates, and building ceramics [3, 4]. For example, when 10% of cement in the light aggregate concrete was replaced with CFA, the increase of binding force was observed resulted in an average of 34% improvement in mechanical properties [5].

Phosphogypsum (PG) is a solid waste generated during the production of phosphoric acid. It contains mainly calcium sulphate dihydrate ($CaSO_4 \times 2H_2O$, >90%), and the remaining are phosphoric acid, sulfuric acid, phosphates, fluorides, traces of metals such as Cr, Cu, Zn, and Cd, and naturally occurring radionuclide radium-226 [6]. Since phosphoric acid is used worldwide in many industrial sectors, for example in the production of cleaning products, cosmetics, and phosphate fertilizers, the constantly increasing demand on phosphoric acid results in a generation of a larger amount of waste PG [7]. Fortunately, waste PG has been mostly utilized in production of binding materials and concrete elements [8–12]. In particular, waste PG has been proved to be an effective mineralizer during roasting of Portland cement clinker [13–18] and it was used as an additive, instead of the natural gypsum, for the controlling of the cement setting time [19–21]. Moreover, one of this paper authors has developed the effective methods of waste PG processing which can be used as a source of gypsum, synthetic resin filler, and additive for paints and lacquers [22–26].

Starch (S) is a natural polysaccharide polymer which is a cheap, widely available, and easily biodegradable. It can be extracted from natural sources such as fruit and vegetable wastes, and from wastes produced by the food, paper and fermentation industries [27-29]. One of the promising applications of the waste recovered starch is the production of building materials [30-32]. For example, when starch was used as a binder of the cement-based composites, they exhibited the increased flowability and setting time, and the low thermal conductivity without significant deterioration of mechanical strength properties [33–34].

The effect of magnetic field on chemical and physical processes has been interesting for a long time. Although the energy of magnetic interactions is low, under specific conditions even the weak magnetic field causes a significant impact on the rate of chemical and electrochemical processes, crystal structure of solids, and physical and chemical properties of the final products of synthesis [35-41]. In particular, in solids, the external magnetic field acts on atoms which is manifested by the higher stress in crystal lattice. On the other hand, in liquids, it affects both electrons and ionized atoms and this develops the dynamic effects [42–44].

In this paper we describe the development of the new cement-based composite with a potential application in construction engineering. The industrial wastes of PG and CFA, and native potato starch dispersed in epoxy resin were used as fillers. The tap water subjected to constant magnetic field with induction of 1 T or non-magnetized tap water was used as batched water of composites. Due the natural radioactivity of PG and CFA, their radiological safety was also evaluated using the gamma-ray spectroscopy. The composites were formulated according to the standards for building materials as trabecular samples, and after one-month curing, they were tested for important properties for use as a construction material, namely, the water absorptivity, the flexural strength, and the compressive strength.

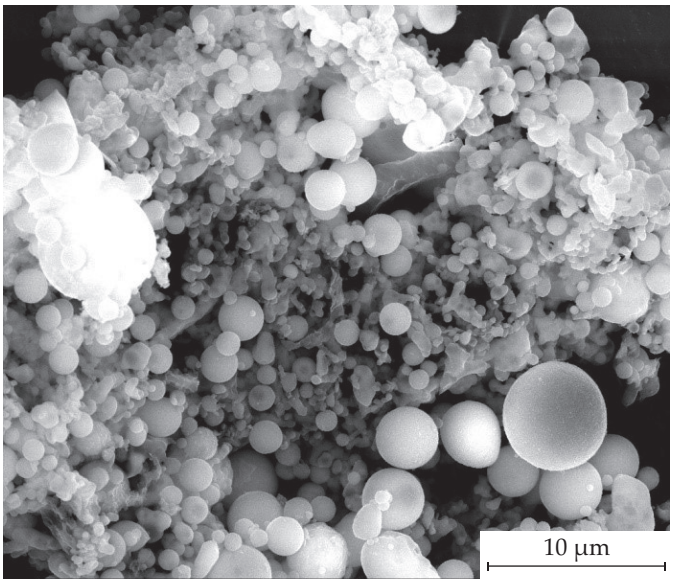

Fig. 1. SEM image of waste CFA from the heat and power plant

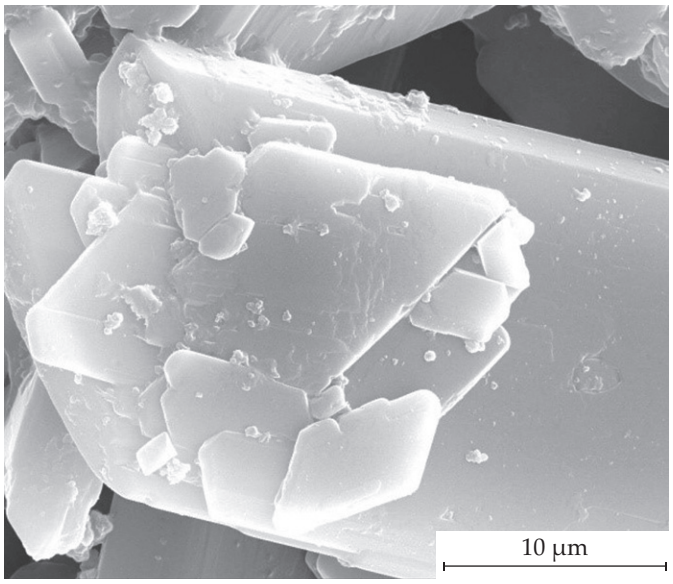

Fig. 2. SEM image of waste PG from chemical plant

EXPERIMENTAL PART

Materials

The following components have been used for preparation of the PC/CFA/PG/EP(S) composites: Portland cement CEM I 42.5 R (Górażdże Cement S.A., Poland) compliant with the PN-EN 197-1 (EN 197-1:2000) standard, waste CFA from the heat and power plant, waste PG from chemical plant, and native potato starch (Chempur, Poland) dispersed in epoxy resin Epidian 5 (Ciech-Sarzyna S.A., Poland). The SEM images of CFA, PG, and EP(S) are presented in Figs. 1–3, respectively.

Methods

Scanning electron microscopy (SEM) images were obtained using the Vega 5135 MM scanning electron microscope (TESCAN, Czech Republic). The impact fracture surfaces of the samples were coated with a thin gold film to avoid charging and to increase image contrast.

Before preparation of composites, the radioactivity of waste CFA and PG was evaluated using the gamma-ray spectrometer equipped with High-Purity Germanium (HPGe) detector cooled with liquid nitrogen and a maximum efficiency of 30% for Pb-210. The samples of waste CFA and PG were dried at temperature of 80 ^{0}C, grinded, and formulated as normalized discs with weight of 15 and 50 g. The measurement time did not exceed 6 h. The measurement uncertainties did not exceed 10% of the measured radionuclide activity. The calibration was verified in accordance with the IAEA 327-Soil standard prepared as normalized discs with weight of 15 and 50 g. The coefficients f_1 and f_2 were used for assessment of the building materials quality [45]. The coefficient f_1 refers to human body exposure to gamma radiation emitted by radionuclides of geological origin such as potassium-40, radium-226, and thorium-228 and it was calculated according to Equation 1:

$$f_1 = 0.00027\ S_K + 0.00027\ S_{Ra} + 0.00053\ S_{Th} \quad (1)$$

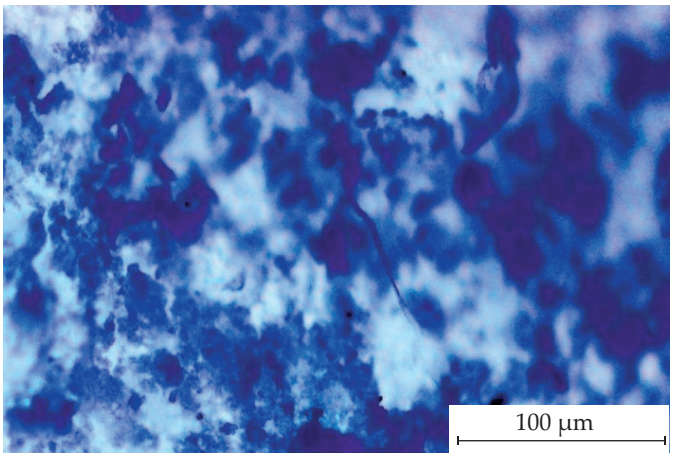

Fig. 3. SEM image of native starch dispersed in epoxy resin (before grinding)

where: S_K, S_{Ra}, and S_{Th} are the activity concentration (in Bq/kg) of potassium-40, radium-226, and thorium-228, respectively. The coefficient f_2 refers to the exposure of pulmonary epithelium to alpha radiation of radium-226, or its derivatives, and it is equal to the activity concentration of radium-226 in Bq/kg (Equation 2):

$$f_2 = S_{Ra} \quad (2)$$

The threshold limits of those coefficients were set up as $f_1 \leq 1$ Bq/kg and $f_2 \leq 185$ Bq/kg [45]. The radioactivities of waste CFA and PG were evaluated in the Institute of Applied Radiation Chemistry of Lodz University of Technology (Łódź, Poland).

As a batched water, the tap water was used. Its chemical composition was determined using Agilent 7100 CE Capillary Electrophoresis System (Agilent Technologies, Santa Clara, CA, USA), and the electrical conductivity was measured with CC-505 digital conductometer (Elmetron Sp.j., Zabrze, Polska). The batched water was magnetized for 0.5 h at room temperature using the constant magnetic field with induction B = 1 T generated by the ER-2525 laboratory electromagnet (Experimental Department of the Polish Academy of Science in Poznań, Poland).

The water absorptivity of the PC/CFA/PG/EP(S) composites was investigated in the following manner. The samples seasoned for one month were weighed on the laboratory balance, and then they were completely immersed in water for 24 h. After 24 h, they were taken out from water, dried with blotting paper at ambient temperature for 0.5 h and weighed. The water absorptivity of composite, A_C, was calculated using the Equation 3:

$$A_C = (w_s - w)/w \times 100\% \quad (3)$$

where: w_s and w (both in g) are the weights of the water absorbed sample and dry sample, respectively. The relative decrease of water absorptivity, ΔA_C, was calculated according to the Equation 4:

$$\Delta A_C = (A_{C(B=0\ T)} - A_{C(B=1\ T)})/A_{C(B=0\ T)} \times 100\% \quad (4)$$

where: $A_{C(B=0\ T)}$ and $A_{C(B=1\ T)}$ are the water absorptivity of composite prepared with non-magnetized and magnetized batched water, respectively.

The mechanical strength of composites was tested using the Zwick-Roell BT1-FR050TH.A1K testing machine for static compression and elongation tests (serial number 156859) with the maximum load of 50 kN equipped with a KAP-TC type force transducer 50 kN (AST Dresden, serial number 156860/5289), bending test rate of 50 N/s, compression test rate of 10 mm/min, and elongation test rate of 50 N/s. Standard trabecular samples with dimensions of 40 × 40 × 160 mm were used. The relative increases of flexural strength, $\Delta\sigma_f$, and com-

pressive strength, $\Delta\sigma_c$, were calculated according to the Equations 5 and 6, respectively:

$$\Delta\sigma_f = (\sigma_{f(B=1\ T)} - \sigma_{f(B=0\ T)})/\sigma_{f(B=0\ T)} \times 100\% \quad (5)$$

$$\Delta\sigma_c = (\sigma_{c(B=1\ T)} - \sigma_{c(B=0\ T)})/\sigma_{c(B=0\ T)} \times 100\% \quad (6)$$

where: subscripts B=1 T and B=0 T refer to the mechanical strength of the composite prepared using magnetized and non-magnetized batched water, respectively.

RESULTS AND DISCUSSION

Radioactivity of CFA and PG

Waste CFA and PG display radioactivity due to presence of naturally occurring radionuclides and their decay products. Thus, to evaluate the radiological safety of waste CFA and PG, the activity concentration of potassium-40, radium-226, and thorium-228 was determined using the gamma-ray spectroscopy. The results of the activity concentration measurements are presented in Table 1.

The radiological safety of waste CFA and PG was evaluated based on the parameters f_1 and f_2 calculated according to Equations 1 and 2, respectively. The calculated parameters f_1 and f_2 were equal to 0.9461 and 103.2 Bq/kg, respectively, for CFA, and to 0.3052 and 44 Bq/kg, respectively, for PG. Since the threshold limits for the parameters f_1 and f_2 were assumed to be $f_1 \leq 1$ Bq/kg and $f_2 \leq 185$ Bq/kg, respectively, it can be concluded that both waste CFA and PG are not radiologically dangerous, and they can be safely used in the original form.

T a b l e 1. Activity concentration A_c of potassium-40, radium-226, and thorium-228 of waste CFA and PG

Radionuclide	A_c, Bq/kg	
	CFA	PG
Potassium-40	510.0 ± 45.0	214.0 ± 7.0
Radium-226	103.2 ± 9.3	44.0 ± 3.0
Thorium-228	123.2 ± 10.3	30.0 ± 2.0

Chemical composition of batched water

The chemical composition of batched water was determined by means of the capillary electrophoresis. The following anions were selected to be determined: Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-}. Both batched water magnetized with CMF with magnetic induction of 1 T for 0.5 h and non-magnetized batched water were tested. The concentration of anions was calculated based on the area under

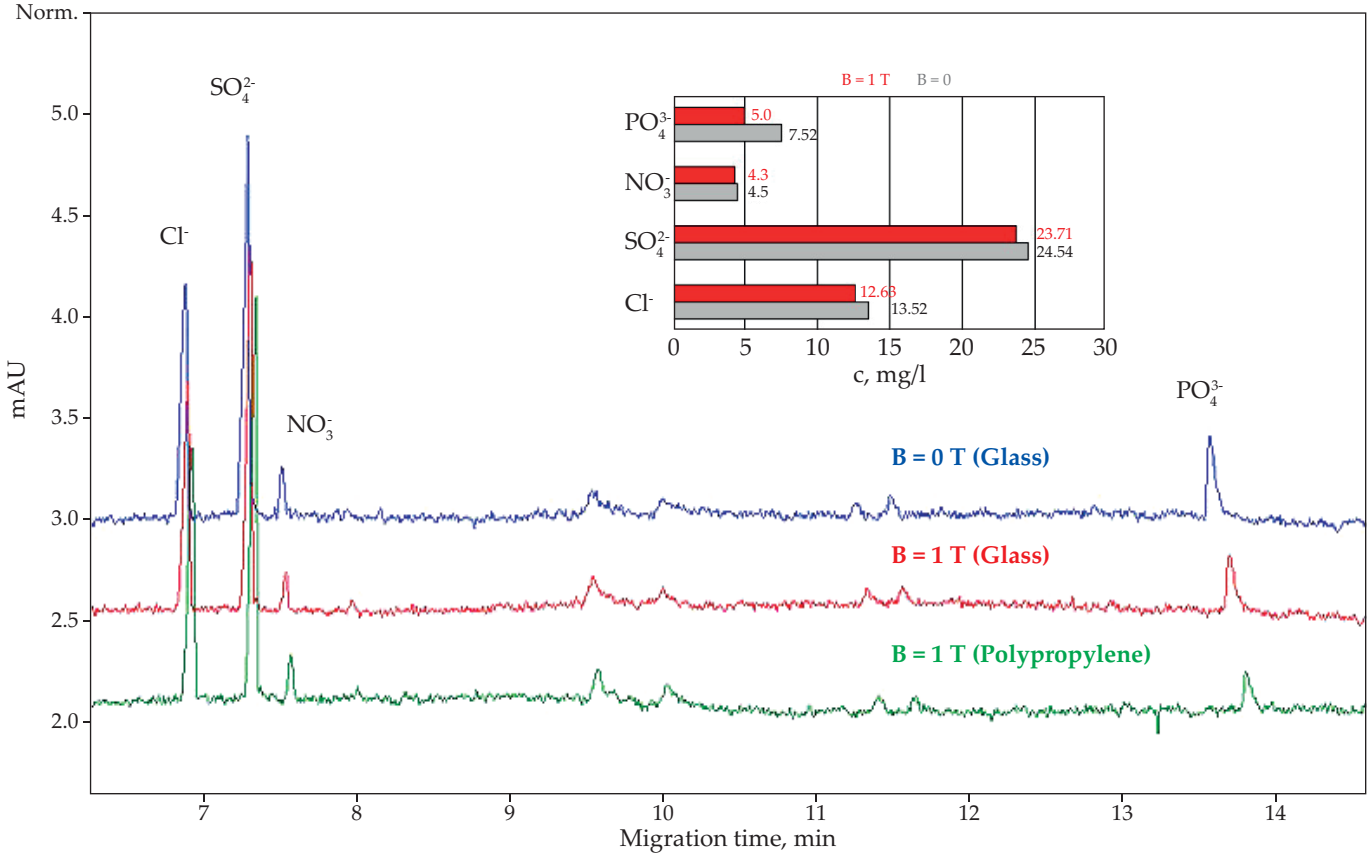

Fig. 4. Electrophorograms of magnetized (B = 1 T, t = 0.5 h) and non-magnetized (B = 0 T) batched water. Inset: concentration of Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-} anions in magnetized and non-magnetized batched water

the peak. Besides the peaks of Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-} anions, other impurities in the matrix were also detected. The results of capillary electrophoresis measurements are presented in Fig. 4.

As it can be seen from the Fig. 4, the concentration of Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-} anions in magnetized batched water was lower than those in non-magnetized batched water.

Electrical conductivity of batched water

The electrical conductivities of magnetized and non-magnetized batched water were tested for two weeks. The average results from three measurements are presented in Fig. 5.

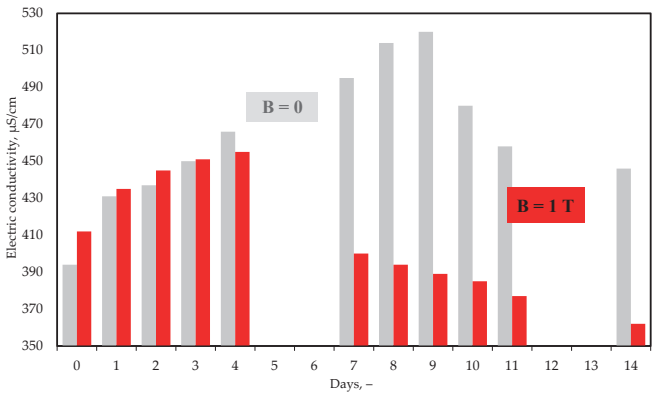

Fig. 5. Electrical conductivity of magnetized (B = 1 T, t = 0.5 h) and non-magnetized (B = 0 T) batched water

Fig. 5 shows that the electrical conductivity of magnetized batched water was higher than this of non-magnetized batched water during the first five days of measurements. However, after seven days, the electrical conductivity of magnetized batched water showed tendency to decrease.

Formulation of PC/CFA/PG/EP(S) composites

The PC/CFA/PG/EP(S) composites were formulated and tested according to following standards: PN-EN 196-1:2005 (Methods of cement testing - Part 1: determination of mechanical strength), PN-B-04500:1985 (Building mortars), and PN-88/B-04300 (Cement). The samples of PC/CFA/PG/EP(S) composites were prepared as follows. Starch was mixed with epoxy resin Epidian 5 and a hardener. After hardening, the resin with a dispersed starch was ground and then mixed with PC, waste CFA, waste PG, and non-magnetized batched water or magnetized batched water treated with CMF with magnetic induction B = 1 T for 0.5 h at room temperature. The average total content of ER(S) and waste CFA and PG in composites was 30% by weight. The curing process of composites took place in moulds with standard dimensions of 40 × 40 × 160 mm. After the curing process has been finished, the composite samples were extracted from the moulds and then air seasoned in the room temperature for one month. Finally, the composite samples were tested for water absorptivity and mechanical strength properties. The SEM images of prepared PC/CFA/PG/EP(S) composites are shown in Fig. 6.

Water absorptivity of PC/CFA/PG/EP(S) composites

Due to the porous structure of cement-based composites, the water absorptivity is a parameter which is very important while considering their application as build-

a) b)

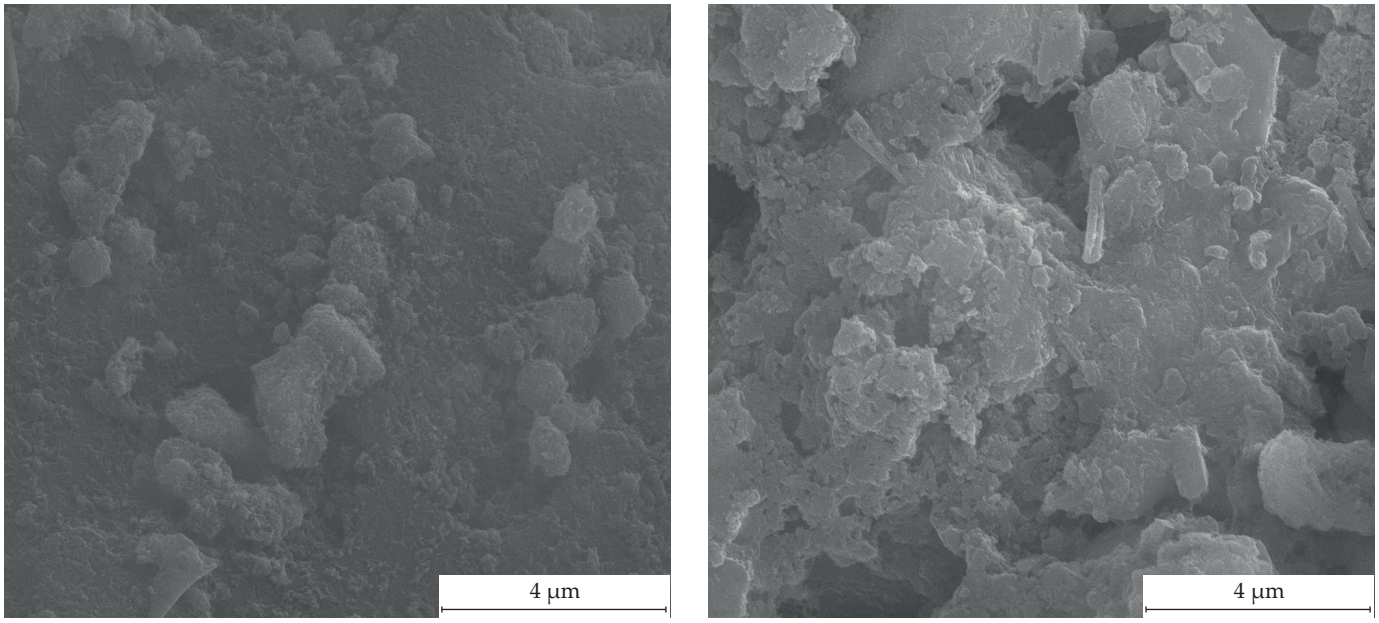

Fig. 6. SEM images of PC/CFA/PG/EP(S) composites prepared using non-magnetized (a) and magnetized batched water (b)

ing materials. The water absorptivity should be as low as possible since it reduces a susceptibility to freezing and penetration into composite of corrosive compounds dissolved in water. Thus, the water absorptivity of the PC/CFA/PG/EP(S) composites was determined using the method in which the weighted samples were totally immersed in tap water for 24 h and reweighted after drying. Water absorptivity A_c and relative decrease of water absorptivity ΔA_c were calculated using Equations 3 and 4, respectively. For comparison, the water absorptivity of homogenous PC was also determined. The results of measurements are presented in Table 2.

T a b l e 2. Water absorptivity A_c and relative decrease of water absorptivity ΔA_c of PC and PC/CFA/PG/EP(S) composites prepared using non-magnetized (B = 0 T) and magnetized batched water (B = 1 T, t = 0.5 h)

Sample	A_c, %		ΔA_c, %
	B = 0 T	B = 1 T	
PC	15.0	12.6	16.0
PC/CFA/PG/BP	20.3	18.8	7.4

Based on the results presented in Table 2 it can be concluded that the water absorptivity of PC/CFA/PG/EP(S) composite prepared using magnetized batched water was lower (A_c=18.8%) than this of prepared using non-magnetized batched water (A_c=20.3%), and consequently, the relative decrease of water absorptivity ΔA_c was equal to 7.4%. Interestingly, the water absorptivity of PC prepared using magnetized batched water was also lower (A_c=12.6%) than this of prepared using non-magnetized batched water (A_c=15.0%) and its relative decrease of water absorptivity was higher (ΔA_c=16.0%) than this of PC/CFA/PG/EP(S) composite(ΔA_c=7.4%).

Mechanical properties of PC/CFA/PG/EP(S) composites

The results of flexural and compressive strengths measurements and their relative increases are presented in Table 3.

As it can be seen from Table 3, the mechanical strength of the PC/CFA/PG/EP(S) composite prepared using magnetized batched water was improved compared to this prepared using non-magnetized batched water. In particular, the flexural strength and compressive strength of the PC/CFA/PG/EP(S) composite prepared using magnetized batched water were 6.1 and 28.9 MPa, respectively, and they were higher than those for the composite prepared using non-magnetized batched water which were equal to 5.7 and 27.6 MPa, respectively. Thereby, the relative increases of flexural strength $\Delta\sigma_f$ and of compressive strength $\Delta\sigma_c$ were 7.0 and 4.6%, respectively. Similarly, the homogeneous CP prepared using magnetized batched water also displayed the improved mechanical strength, namely, its relative increase of flexural and compressive strengths were 11.9 and 6.6%, respectively.

CONCLUSIONS

The aim of the study presented in this paper was to investigate the possibility of utilization of biopolymer S dispersed in synthetic epoxy resin and waste CFA and PG to obtain the cement-based composite building material. The result of our investigations clearly show that it is possible to prepare the cement-based composite using S dispersed in EP and waste CFA and PG as fillers with improved properties in terms of potential use as a building material. The PC/CFA/PG/EP(S) composite prepared with magnetized batched water in constant magnetic field with induction B = 1 T for 0.5 h showed the reduced water absorptivity by 7.4%, and the increased mechanical flexural strength and the mechanical compressive strength by 7.0 and 4.6%, respectively, compare to the composite prepared with non-magnetized batched water. In addition, when the homogenous PC was prepared with magnetized batched water, it also exhibited the lower water absorptivity and the higher flexural and compressive strengths. Since the utilization of waste materials is strongly recommended in the view of both depletion of natural resources and the environmental protection, we hope that the presented procedure will allow recycling of waste CFA and PG which large amounts are stored in landfills worldwide.

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T a b l e 3. Flexural strength σ_f, compressive strength σ_c, and their relative increases $\Delta\sigma_f$ and $\Delta\sigma_c$, of standard trabecular samples of PC and PC/CFA/PG/EP(S) composites prepared using non-magnetized (B = 0 T) and magnetized batched water (B = 1 T, t = 0.5 h)

Material	σ_f, MPa		$\Delta\sigma_f$, %	σ_c, MPa		$\Delta\sigma_c$, %
	B = 0 T	B = 1 T		B = 0 T	B = 1 T	
PC	7.6	8.5	11.9	41.1	43.8	6.6
PC/CFA/PG/EP(S)	5.7	6.1	7.0	27.6	28.9	4.6

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