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Influence of Expanded Graphite Surface Ozonation on the Adhesion between Carbon Additive and Cement Matrix

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Cement mortars modified with expanded graphite (EG) subjected to surface treatments in gaseous ozone were investigated. It was shown that the bonding between the carbon additive and cement paste strongly depends on the surface modification of EG and the chemical composition of the EG surface. As a result of the ozone treatment on the EG surface, mostly oxygen functional groups of phenol, carbonyl and carboxyl types was emerged. Moreover, in the case of EG subjected to ozone treatment, foliation of its structure was observed. These factors play an important role in shaping better adhesion of oxidized EG to the cement matrix. As a result, a substantial increase in flexural toughness of the cement composite with ozonized EG was observed. The above results were confirmed by XPS and SEM analysis.

Keywords: cement composites, expanded graphite, surface treatment, adhesion, mechanical properties.

1. INTRODUCTION

In recent years, many papers in the field of cement mortars and concrete modified with additives like carbon fibres, expanded graphite or nanoparticles have been published [1 – 4]. Due to the distinctive properties of such additives, cement composites with novel functions can be created. Besides the improvement of flexural toughness, carbon additives can enhance the electrical and thermo-electrical properties of the cement matrix, which make such structures very attractive from the applicable point of view [5 – 8]. Cement composites modified with carbon additives can be used for example in electromagnetic interface shielding, electrostatic discharge, self-regulated heaters, conductive floor panels or stress/strain sensors for damage assessment [9 – 10].

Among all the factors influencing the bonding between different types of fibers and the cement matrix, the most important are mechanical interlocking and chemical interaction [11 – 12]. Mechanical interlocking enhancement of fibers in the cement matrix can be achieved by a higher l/d factor, changes in the fiber cross-sections or the usage of fibres with hooked ends. However, relatively little attention has been paid in literature to the role of fiber surface characterization in shaping the properties of cement composites. The small dimensions of carbon materials, especially expanded graphite, causes that in the case of these materials, the chemical interaction between the carbon surface and cement matrix will be the main factor promoting increased strength of such a composite. The chemical character of the carbon surface depends largely on the structure of the original material and on the method of surface oxidation. Choosing the right method of oxidation can shape the following properties of the carbon material like developed specific surface area, porous structure, high level of surface oxidation or all those features simultaneously. The carbon surface can be modified by oxidation in the gaseous or liquid phase. The modification of carbons in the gaseous phase can be performed either at a high temperature (above 950 °C) in a neutral atmosphere or in vacuum; or in milder conditions, through oxidation at temperatures below 900 °C in a stream of air or oxygen. Oxidation in the gas phase can also be achieved with the help of other oxidizing media, for example: steam, carbon dioxide or ozone [13 – 14].

When the carbon additives like EG have very small dimensions, the physical interaction between the additive and cement paste is very weak. Therefore, chemical modification can be applied in order to build oxygen functional groups of hydroxyl or carboxyl type on the surface of the carbon additive. Acidic functional groups give the EG surface a hydrophilic character, which increases their adhesion to the cement paste. The improvement of EG wettability as a result of chemical treatment also has a practical meaning in the process of cement-carbon composite preparation. Carbon materials can be dispersed in the cement matrix in two ways: either by mixing with other composite ingredients first in the dry state and then with water, or by initial dispersing in water and mixing them with the other composite ingredients in a mixer. The second way is possible after changing the carbon materials surface character from hydrophobic to hydrophilic, as a result of chemical surface modification.

In contrast to previous work, in the present studies the influence of oxidation treatment of EG on the adhesion to the cement matrix is investigated. The surface treatment of EG was performed by means of gaseous ozone. The chemical composition of the EG surface, untreated and subjected to ozone modification, was verified by means of X-ray photoelectron spectroscopy (XPS) analysis, whereas the changes in the EG morphology and cement composites microstructure modified with EG were tested using

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scanning electron microscopy (SEM). The evaluation of adhesion between EG and the cement mortars was tested based on the pre-crack behavior of the cement composites.

2. EXPERIMENTAL PROCEDURE

Expanded graphite (EG) was synthesized by thermal exfoliation of a stage-4 graphite intercalation compound with sulfuric acid (H_2SO_4-GIC). The process of exfoliation was performed in a muffle furnace at the temperature of 800 °C for 4 min. H_2SO_4-GIC used for exfoliation was prepared by anodic oxidation of graphite powder, with particles 32 μm to 71 μm in diameter, in 18 M H_2SO_4 [15].

The EG ozone oxidation process of was performed under a continuous flow of gaseous ozone through a bed of expanded graphite, beforehand placed into a glass reactor. The ozone was produced from air in an ozone generator. The stream of ozone was passed through the EG for one hour at a constant flow rate of 2 $dm^3 min^{-1}$. The reactions between EG and ozone were carried out at room temperature. The obtained material (denoted as EG-O) was used to prepare the cement composite.

The cement composites were made from cement CEM I 42.5R, quartz sand (0/0.5 mm), fly ash and distilled water in the relation 1 : 0.9 : 0.1 : 0.5, respectively. In order to improve the workability and decrease the porosity of the cement composites, butadiene-styrene copolymer in the amount of 25 kg/m^3 was used. The EG, and EG-O were added to the cement matrix in the amount of 0.5 wt.% in relation to the mass of cement. The mixing process was performed according to the following procedure. In the first step, the cement was mixed with fly ash and quartz sand. Then the unmodified or modified expanded graphite was added. In the last step, the water and latex were added, and all components were mixed and then poured into oiled moulds. For each series, 5 specimens with dimensions of 1 : 1 : 6 cm were made. The samples were demolded after 24 h and stored in water till the mechanical tests after 56 days of hardening were performed.

A Zwick/Roell press type Z020 was used in order to determine the mechanical parameters of the cement mortars (Fig. 1). The value of stress in relation to displacement at constant rate of 0.1 mm/min was recorded by means of three-point bending tests. The flexural toughness of the composites was calculated as the area below the stress-strain curve in the pre-crack region.

Fig. 1. Three-point bending test of cement composites

The changes in specific surface area effected by the ozone treatment of EG were determined from the isotherms measured by N_2 adsorption at 77 K with an ASAP 2010 apparatus and calculated using the BET equation.

The surface chemical composition of the original and ozone treated EG was estimated by XPS analysis. The X-ray photoelectron spectroscopy (XPS) measurements were realized with an ESCALAB 210 spectrometer (VG Scientific, East Grinstead, UK) using non-monochromatized Al K_α radiation (1486.6 eV). The attained XPS spectra were analyzed by performing Shirley-type background subtraction and using a Gaussian-Lorentzian mix function of a 70 % / 30 % ratio. The binding energy scale was corrected by referring to the graphitic peak at 284.5 eV.

The analysis of the morphological and textural properties of EG due to its interaction with ozone (EG-O sample) as well as the EG-O/mortar composites were studied by scanning electron microscopy (SEM) (Evo40, Carl Zeiss microscope) using an acceleration voltage of the electron beam adjusted to 17 keV.

3. RESULTS AND DISCUSSION

It is widely known that the ozone treatment of carbon materials leads to a considerable increment in their degree of oxidation due to the formation of oxygen functional groups. The types of oxygen bonds with carbon atoms as well as their concentration mainly depend on the type of carbon material that underwent ozonation and the conditions under which the ozone treatment is performed. Among the oxygen functionalities during carbon ozonation, carboxylic, hydroxyl, ether, carbonyl and on a much smaller scale lactone groups, are commonly generated [16 – 17].

The XPS analysis of the interactions between the gaseous ozone and expanded graphite undoubtedly confirm the above mentioned information. From the comparison of the chemical composition of the EG surface before and after ozone treatment (data given in Table 1) it is seen that the surface oxygen concentration considerably increases. The total amount of oxygen for the ozonized (–EG–O–) is almost 5 times higher compared to the original EG. The O 1s spectrum for both samples comprises 3 signals appearing at 532.1 eV – 532.2 eV, 533.4 eV – 533.7 eV and 534.7 eV – 535.0 eV. According to the literature data, the regarded peaks can be ascribed to oxygen pertaining to C=O, C–O species and chemisorbed oxygen or/and adsorbed water, respectively [18 – 20]. As seen in Table 1, the concentration of all the oxygen peaks considerably increases after the ozone treatment of EG. The increased concentration of surface oxygen due to ozonation in some aspects coincides with the data revealed from the C 1s spectra. Particular analysis of these spectra indicates that the ozone treatment of EG results in the increment of C=O species (peak at binding energy about 287 eV). Simultaneously, the number of C–O bonds (peak at binding energy about 285.8 eV drops considerably for the EG-O sample (Table 1) as a consequence of ozone treatment. According to some authors, the observed features can be explained in terms of transformation of C–O species into C=O containing functional groups [21 – 22]. The difference between the total surface oxygen calculated from the O 1s spectrum and oxygen bonded with carbon atoms noted from C 1s might be partially elucidated in terms of the appearance of ozone unbounded with carbon or/and oxygen being a product of its decomposition remaining within the structure of ozonized EG [13]. Besides changes in the chemical composition, the intensive reactions of gaseous ozone with carbons, may also result in modification of their crystalline and porous structure. The considered structural modifications are accompanied by the formation of CO and CO_2 followed by their evaporation [21 – 22].

Table 1. Surface composition for EG before and after ozone oxidation (EG-O) determined from XPS analysis

Spectrum	(eV)	(at.%)	Total content (at.%)	Assignment
Original EG				
O 1s	532.1	0.8	3.3	O=C
	533.4	1.2		O–C
	534.7	1.3		chemisorbed oxygen/water
C 1s	284.6	61.1	96.7	C–C (graphitic)
	285.9	20.7		C–O
	287.3	8.3		C=C
	290.7	6.6		delocalized π electrons
EG-O				
O 1s	532.2	4.3	16.6	O=C
	533.7	6.2		O–C
	535.0	6.1		chemisorbed oxygen/water
C 1s	284.6	50.4	83.4	C–C (graphitic)
	285.8	14.2		C–O
	287.0	13.8		C=C
	290.4	5.0		delocalized π electrons

In presented work, the above mentioned hypothesis is confirmed by the significant development of specific surface area. The BET surface area increases from 30.5 m^2/g for the original EG to 36.1 m^2/g for the EG sample that underwent ozone treatment (EG-O). Moreover, as is seen in Fig. 2 depicting the SEM image of ozonized EG, the morphology of EG is considerable altered due to its interactions with ozone.

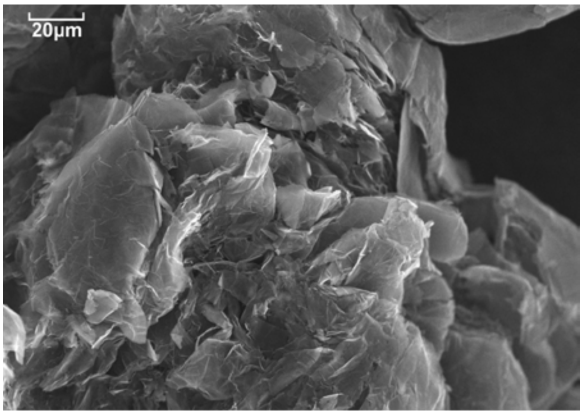


Fig. 2. Surface of ozonized EG

From the comparison of SEM images of EG before (Fig. 3) and after ozone treatment (Fig. 2), it is seen that the EG-O structure is significantly destroyed. Within the graphene layers some damages, like shortening of the graphene edges are observed. Summing up, it can be pointed out that the ozonation of EG likely results in a higher amount of surface defects. Such a feature with relation to enlarged concentration of surface oxygen makes ozonized expanded graphite much more chemically active than original EG and thus more attractive from the practical point of view.

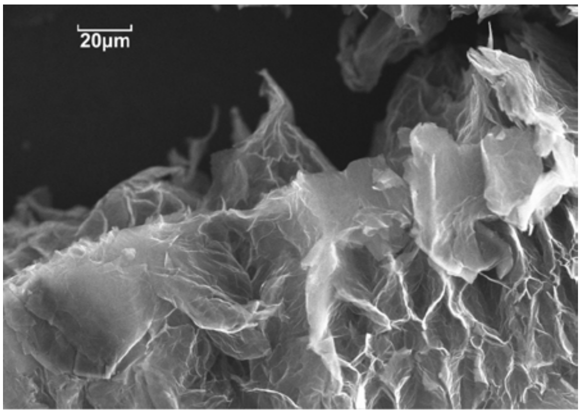


Fig. 3. Surface of untreated EG

In Figure 4, exemplary relation curves of stress versus displacement of cement-carbon composites pure and modified with as-received and ozone oxidized EG are presented.

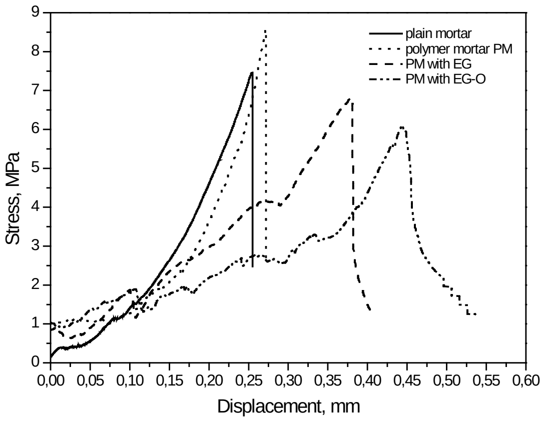


Fig. 4. Stress-displacement dependences recorded for cement composites modified with pure and ozone-treated expanded graphite

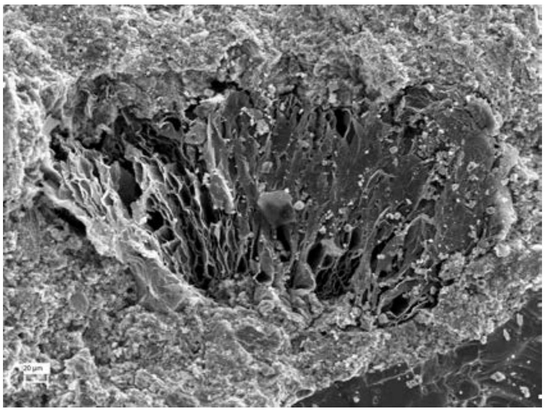
Their comparison indicates that in the case of such materials the load is mainly transmitted by the cement matrix and there is no growth of the total bending resistance of the cement-carbon composite. The effect of the EG additive is visible only in comparison of the time needed for a total break of the cement specimens. In the case of EG after oxidation in ozone, the time needed to destroy the cement specimens is longer than for the cement specimens with unmodified EG and for mortar without EG additive. The analysis of the load curves in the displacement function leads to the conclusion that the gradient angle of the curve also changes depending on the carbon addition applied. In the case of cement mortars modified with EG oxidized in ozone, the gradient is the smallest, thus the cement-carbon composite is the most resistant to the bending load. It is indirect proof that as a result of chemical modification on the surface of carbon materials, oxygen functional groups are built that enable chemical bonding with the cement paste and improve the flexural toughness of the composite [2, 23]. Despite the smaller number of EG in cement mortar, the cracking resistance of the composite is improved, but the mechanism of those materials is a bit different. The effect of the EG additive is visible on the curve load-displacement in the elastic area of the cement matrix, and not as in the case of longer fibres, after its break. In the case of a small amount of carbon additive, the load is carried by the cement matrix. During a rise in load, the first microcrack appears in the cement matrix, which gradually develops into a crack and consequently leads to breakage of the cement sample. If there is a graphite flake on the path of micro-crack, part of the load will be used to stretch it and, in the end, to extract it from the cement matrix or to break it. It is indicated by a smaller gradient of the load curve in the displacement function and by longer time needed to break the cement specimen, which results in higher resistance to the bending load of such mortar.

The data presented in Table 2 confirm the above statement. An increase in ultimate flexural strength was observed for the mortars modified with latex dispersion, while, deterioration of the flexural strength values was noticed in the case of cement composites modified with EG and EG-O. On the contrary, the polymer mortar modified with expanded graphite subjected to ozone treatment showed the best resistant to loading. In this case, the highest values of flexural toughness and elongation at break were noticed. The others samples cracked in the same way, nevertheless, the flexural toughness and deflection values were lower.

Table 2. Selected mechanical properties of cement composites with and without EG

	Flexural strength, MPa	Flexural toughness, MPa·mm	Elongation at break, mm
Plain cement mortar	6.9 ±0.5	0.589 ±0.208	0.16 ±0.04
Polymer cement mortar PM	10.2 ±2.3	0.690 ±0.085	0.37 ±0.08
PM with EG	6.7 ±1.1	0.984 ±0.256	0.58 ±0.18
PM with EG-O	6.9 ±0.9	1.193 ±0.238	0.69 ±0.21

The results of the mechanical parameters are consistent with the SEM observation of the composite microstructures presented in Figures 5 and 6. It was shown that in the case of the cement mortars with unmodified EG (Fig. 5, a, b), the graphite flakes do not change the shape. Moreover, the interfacial transition zone between the EG surface and cement pastes indicates discontinuity in some places and therefore weaker adhesion to the cement matrix. In contrast, the cement mortar modified with EG subjected to ozone treatment exhibits a substantial change in the character of the graphite flakes. Ozone activation, apart from alternating the oxidation level of the carbon materials surface, can also influence the selective growth of the



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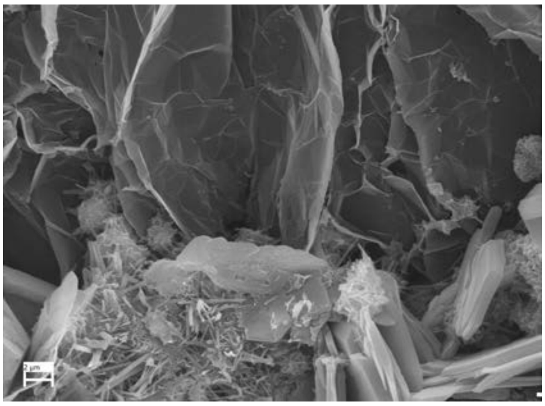
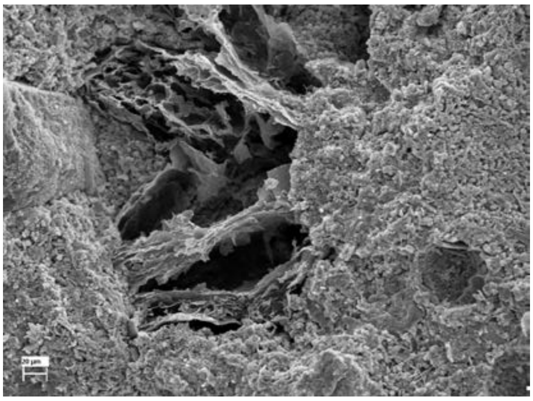


b

Fig. 5. SEM image for cement composite with untreated expanded graphite



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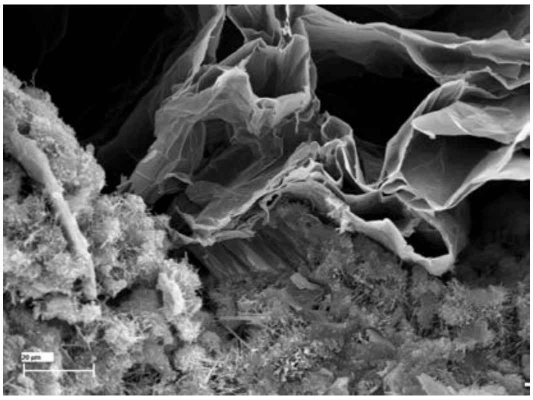

b

Fig. 6. SEM image for cement composite with ozone treated expanded graphite

porous structure of the carbon materials. As mentioned earlier, the ozone treatment of expanded graphite causes partial destruction of the EG structure and introduces some defects to the graphene sheets (Figs. 2 and 6, b). Moreover the EG structure, as can be seen in Fig. 6, b, undergoes foliation. Indirect confirmation of above phenomena is the significant decrease in bulk density of EG subjected to ozone treatment. The bulk density changes from 0.035 g/cm^3 for untreated EG to a value of 0.017 g/cm^3 for the ozonized one. Therefore, the expanded graphite is more susceptible to foliation into separate sheets during mixing with the other components of the cement matrix, and the graphene layers are easily enclosed by the products of cement hydration (Fig. 6, a). It contributes to better adhesion of the expanded graphite to the cement matrix and higher flexural toughness of the composite.

4. CONCLUSIONS

In the presented research, EG added to the cement matrix is characterized by a low shape factor in comparison with commonly used short carbon fibres in composite technology, thus their addition to the cement mortar does not cause an increase in flexural strength. However, it was shown that EG and EG modified in ozone played a much more important role in shaping the mechanical properties of the composite in the pre-cracking zone by increasing its resistance to bending load. Interesting results were achieved for the cement mortars with EG modified in ozone due to its tendency to foliation. As a result of EG surface oxidation in ozone, the EG morphology was considerably altered. Within the graphene layers some damages, like the shortening of graphene edges were observed. Such a feature with relation to the enlarged concentration of surface oxygen caused the expanded graphite to be much more susceptible to foliation into separate sheets during the making of the cement composites and can be easily enclosed by the products of cement hydration. Moreover, the higher concentration of oxygen groups on the EG surface led to better dispersion of the carbon material in the cement matrix and gave better adhesion of the EG flakes to the cement paste. The consequence of above feature was an increase in flexural toughness of the composite.

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