

Influence of expanded graphite coming from the electrochemical oxidation of phenol on cement-polymer matrix

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In presented article the polymer-modified cement mortars with expanded graphite covered by the oligomer film, being a by-product of phenol electro-oxidation, were investigated. The changes in the morphology of EG and EG/oligomer as well as in the microstructure of cement-polymer composites modified with EG/oligomer were verified using the scanning electron microscopy (SEM). The evaluation of adhesion between EG/oligomer and cement-polymer mortar based on the mechanical tests, especially their flexural behavior. It was shown that the oligomer film formed on EG surface made graphite flakes more durable and resistant to bending. Moreover, the oligomer due to the interaction with polymer network in cement-polymer mortar led to the improvement of flexural toughness of composite.

Keywords: cement-polymer matrix, expanded graphite, surface treatment, adhesion, mechanical properties.

INTRODUCTION

Wastewater produced in many industrial processes includes various carcinogens and toxic, non-biodegradable organic substances which should be removed from water before its reused. One of the way of purification of hazardous water is the chemical or electrochemical depollution which is a very efficient and economic method. The wastewaters are usually oxidized with ozone or by using hydrogen peroxide in the presence of Fe^{+2} as a catalyst. The chemical oxidation method almost completely eliminates organic pollutants from the water, but the removal of total organic carbon is impossible and still remains a problem. Therefore, the electro-oxidation of the hazardous pollutants from wastewater has been extensively studied during the recent years. In the electrochemical oxidation, the organic compounds adsorbed on the surface of anode are converted to carbon dioxide which can be easily removed¹⁻⁴.

One of the anode processes which is conventionally used to remove organic pollutants from sewage is the electrochemical oxidation of phenol. It is well known that completely electrochemical oxidation of phenol leads to CO_2 and water but this process proceeds through the several steps in which variety of intermediate products of different features are generated. Among them, the formation of oligomer film covering the surface is recognized as the most important problem of the process of phenol electro-oxidation. Due to its insufficient electrochemical activity, low conductivity and insolubility in water-electrolytes the layer of oligomer hinders the access of phenol molecule to active sites which are localised on the surface of electrode material. In consequence, the proceeding process may be considerably inhibited or/and even in some cases entirely interrupted. The thickness of oligomer film as well as the rate of its formation depend on the method and conditions under which the electrochemical oxidation of phenol is performed^{2, 5-6}. In most cases due to the insufficient electrochemical activity, very low electrical conductivity, and high adhesion, oligomer layer causes the EG electrode inactivated, which becomes completely useless from the electrochemical point of view. Numerous treatment techniques have

been developed to overcome the problem of electrode deactivation by polymer products formed on its surface. One of them was based on the finding the appropriate conditions of phenol electro-oxidation. Another way of investigations was focused on finding the effective method of electrode regeneration enabling their reuse^{7, 8}. In the opposite to above ways of EG/oligomer regeneration and reuse, in the present research the practical application for this material was proposed, namely as an additive to cement-polymer matrix. It is well known that cement matrix is brittle and exhibits very poor tensile and flexural strength. One of the way of improving above disadvantages is polymer modification. In addition, the polymer modification of cement matrix improves adhesion of polymer-cement paste to aggregate and lowers porosity in the interfacial transition zone between cement paste and aggregate giving the more durable structure^{9, 10}. The flexural strength and toughness of cement based composites can be improved by the addition of particles or fibers, including carbon-based materials, as well^{11, 12}. In our previous work, the pure expanded graphite and ozone – modified expanded graphite were added to the pure cement mortar. It was shown that during the chemical modification of EG surface the increase of functional groups like carboxylic or hydroxyl occurred causing the increase of flexural parameters of cement mortars^{13, 14}. In case of EG covered by the oligomer film the oxide functional groups on the surface are blocked, and therefore, in the presented research the more compatible polymer-cement mortar were applied.

MATERIALS AND METHODS

Synthesis of expanded graphite

Expanded graphite (EG) was synthesized by thermal exfoliation of a stage-4 graphite intercalation compound with sulfuric acid ($\text{H}_2\text{SO}_4\text{-GIC}$). The process of exfoliation was performed in a muffle furnace at the temperature 800°C for 4 min. $\text{H}_2\text{SO}_4\text{-GIC}$ used for exfoliation was prepared by anodic oxidation of graphite powder, with particles 32 to 71 μm in diameter, in 18 M H_2SO_4 ¹⁵.

Synthesis of expanded graphite/oligomer composite

Oligomer being a by-product of incomplete oxidation of phenol was deposited onto the expanded graphite surface forming EG/oligomer composite by electrochemical method. The process of electrochemical oxidation of phenol was realized in three-electrode cell by cyclic voltammetry method using expanded graphite as a working electrode. The working electrode was prepared according to the following procedure. The powder type EG was placed into the pocket made of porous polymer in which the graphite rod (5 mm in diameter and 50 mm in length) playing a role of current collector was beforehand inserted. Afterward, the working electrode was immersed into the electrochemical cell filled with 0.1 M phenol dissolved in 0.5 M aqueous KOH and rested to stay in an open circuit for 30 min for equilibration. During the process of phenol electro-oxidation, the potential was scanned at the rate 0.1 mV s^{-1} within the potential range from the rest potential of working electrode (ER) to 0.8 V. Besides the working electrode, the electrochemical cell was composed of a Hg/HgO/0.5 M KOH (+0.117 V vs. NHE) as a reference electrode and graphite rod (5 mm in diameter and 50 mm in length) used as a counter electrode.

After the third cycle of phenol oxidation, the process was interrupted and the sample EG coated with oligomer product of phenol oxidation (EG/oligomer) was taken out from the electrolytic cell, rinsed with distilled water and rested to stay in air for drying. Thus prepared composite material was used for the preparation of polymer-cement composites.

Synthesis of cement-EG composites

The cement composites was made from cement CEM I 42,5R, quartz sand (0/0.5 mm), fly ash and distilled water in relation 1:0.9:0.1:0.5, respectively. In order to improve workability and decrease the porosity of cement composites, latex (butadiene-styrene copolymer) in the amount of 25 kg/m^3 were used. EG/oligomer were added to 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, cement were mixed with fly ash and quartz sand. Then the EG/oligomer was added. In the last step, the water and latex emulsion 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. Samples were demolded after 24 h and stored in water till the mechanical tests were performed.

Analysis and equipment

The electrochemical measurements were carried out using AUTOLAB potentiostat-galvanostat (model PGSTAT 30) supplied by EcoChemie. The analysis of morphological and textural properties of EG and EG/oligomer composite as well as the composites EG/oligomer/polymer mortar were studied by scanning electron microscopy (SEM) (Evo40, Carl Zeiss microscope) using an acceleration voltage of electron beam adjusted to 17 keV. The mechanical parameters of cement composites were determined by means of the Zwick/Roell press type Z020. The three-point bending tests at a constant

rate of 0.2 mm/min were used to measure the stress-displacement dependence.

RESULTS AND DISCUSSION

Electrochemical oxidation of phenol on EG

Figure 1 displays cyclic voltammograms recorded during the process of phenol electro-oxidation at electrode made of the original EG. During the first cycle of oxidation the well-defined anodic peak can be seen at the potential of 0.46 V. On the basis of our knowledge, the regarded peak can be ascribed to the reaction of phenol oxidation^{7, 8}. For the second and third cycle the intensities as well as current charges of the regarded peak markedly fell down due to formation of oligomeric products on the surface of EG electrode. The decrease in the intensity of phenol oxidation peak after the first oxidation cycle establishes in a worsening of electrochemical activity of EG electrode and leads to the inhibition of the phenol electro-oxidation reaction in the subsequent cycles. Depending on the pH of electrolyte, the beginning of the process of phenol oxidation includes the generation of phenoxy radicals in acidic solution and phenolate ions in alkaline media. During the first step of process performed in alkaline media phenolate ions are transformed into phenoxy radicals¹⁶. Phenoxy radicals can be oxidized to complete electrochemical conversion of phenol, which may proceed through the formation of aromatic (hydroquinone, benzoquinone) and aliphatic (maleic, fumaric and oxalic acids) intermediates. According to the alternative pathway, phenoxy radicals react with another radicals or unreacted ions yielding dimeric products^{17, 18}. The dimeric compounds undergo coupling reactions giving compounds of a longer chain and increased mass. The created oligomeric structures may be linked between each other through the etheric bonds. The appearance of C-O as well as C=O bonds within the oligomeric products of incomplete process of phenol electrooxidation are revealed by the literature data^{17, 18} and our previous investigations^{3, 4, 7, 8}.

The presence of oligomer film covering the porous structure of expanded graphite flakes is proved by the almost three-fold decrease in BET surface area. The specific surface area decreases from $30.5 \text{ m}^2/\text{g}$ for the

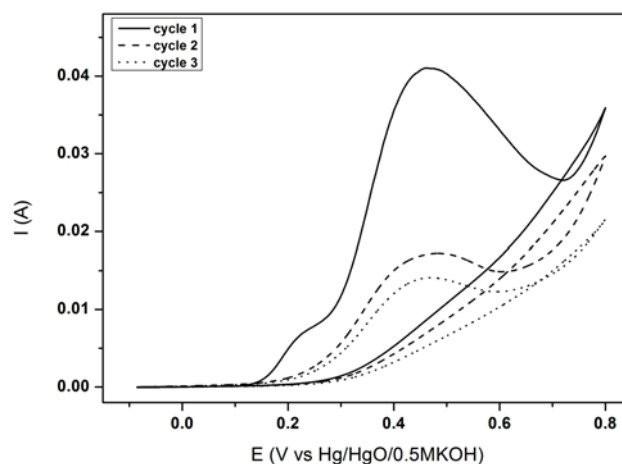


Figure 1. Cyclic voltammograms for EG recorded in 0.1 M phenol in 0.5 M KOH in the potential range $ER \leftrightarrow 0.8 \text{ V}$ with scan rate 0.1 mV/s , mass of electrode 50 mg

original EG to $7.1 \text{ m}^2/\text{g}$ noted for sample EG after the three cycles of phenol oxidation due to oligomer layer. Another proof of a oligomer occurrence on the surface of EG is given from the comparison of SEM images recorded for original EG (Fig. 2a) and EG after the three cycles of phenol electro-oxidation (Fig. 2b). As can be seen in Figure 2, the expanded graphite has a harmony-like structure, resulting from the cleavage and wrinkling of graphite flakes. Characteristic feature of this material is the appearance of sharp edges of graphite flakes. The electrochemical treatment in which the oligomer film was deposited on the EG surface results in partial destruction of graphene layers. The graphite plates of EG/oligomer becomes more wrinkled and their splitting spreads into all graphene layers. From the Figure 2b it is seen that the electro-oxidation of phenol proceeds within the all regions of EG surface thus the layer of oligomer covers the entire graphene layer of EG.

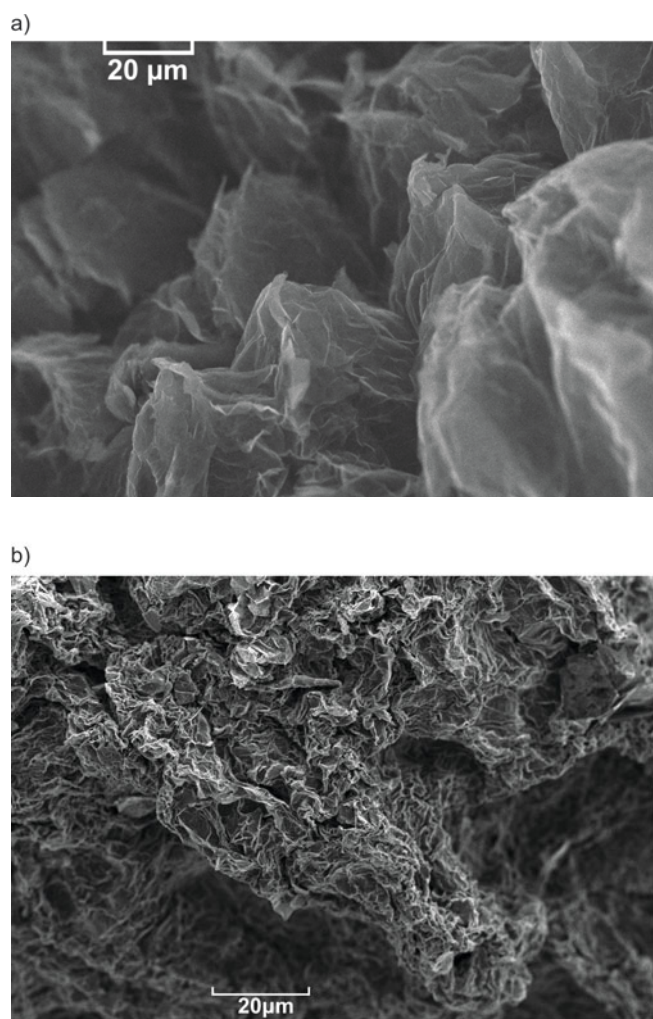


Figure 2. a) Surface of untreated EG; b) Surface of EG covered by oligomer

Mechanical characterization of EG modified cement composite

It is known that the polymer-cement matrix can be created by introducing polymer, oligomer or monomer to the cement mortar or concrete. In the case of polymer-cement matrix polymerized before mixing (e.g. latex emulsion) the setting of mortar occurs by the two processes: the hydration of cement phases and the formation of continuous polymer film. As a result of

described processes, the polymer-cement microstructure is formed with two interpenetrating nets: polymer and cement what is well seen in Figure 3. The presence of both nets results in the better flexural strength of cement-polymer composites and better compaction of composite microstructure. The results of mechanical properties obtained for cement mortar and latex modified mortar are shown in Table 1. It was observed that the polymer additive increased the flexural strength of cement mortar, and significantly improved flexural toughness of composite. These effects are consistent with results obtained by others scientists^{19, 20}.

Table 1. Results of mechanical properties for cement mortar and latex modified mortar

	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 mortar PM	10.2 ± 2.3	0.690 ± 0.085	0.37 ± 0.08
PM + EG/oligomer	10.4 ± 0.9	0.938 ± 0.238	0.41 ± 0.21

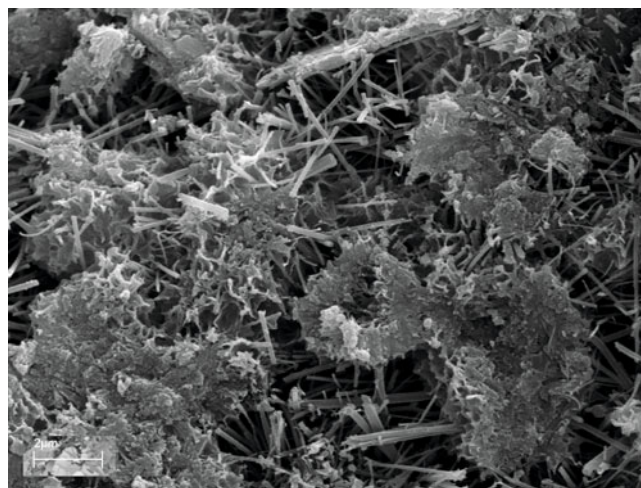


Figure 3. SEM spectrum for polymer-cement mortar (two interpenetrating nets arose from polymer and cement phases hydration)

The influence of EG covered by the oligomer film on the mechanical properties of cement-polymer mortars was shown on the Figure 4. The presence of EG/oligomer in cement-polymer mortar caused the increase of flexural strength and elongation at break of composite. In this case there was also observed the substantial increase of flexural toughness of composite defined as the area below the load-displacement curve. Both, the pure cement mortar and cement-polymer mortar cracked in the same way; nevertheless, the values of flexural toughness's and deflections were lower. The increase of resistance to bending for cement-polymer mortar with EG/oligomer resulted probably from the chemical interaction between oligomer layer localized on the EG surface and polymer net occurring in the cement mortar.

The results of mechanical parameters are consistent with SEM observation of composite microstructure, which is presented in Figure 5. It was shown that in the case of cement-polymer mortars with EG covered by oligomer film graphite flakes does not change their shape. Moreover, the very good adhesion between polymer-cement mortar and graphite flakes was observed

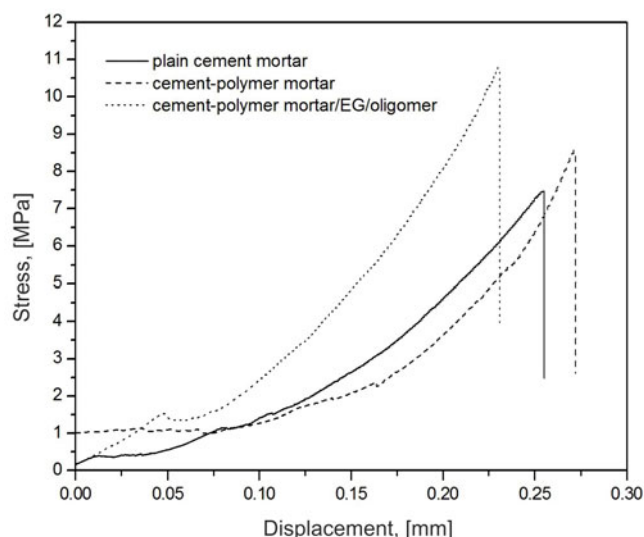


Figure 4. Stress-displacement dependences recorded for plain cement mortar and polymer mortars with and without EG/oligomer

on the SEM spectra. It confirms that the oligomer film formed on EG surface shows the chemical affinity to polymer network and makes the polymer-cement mortar more resistant to bending.

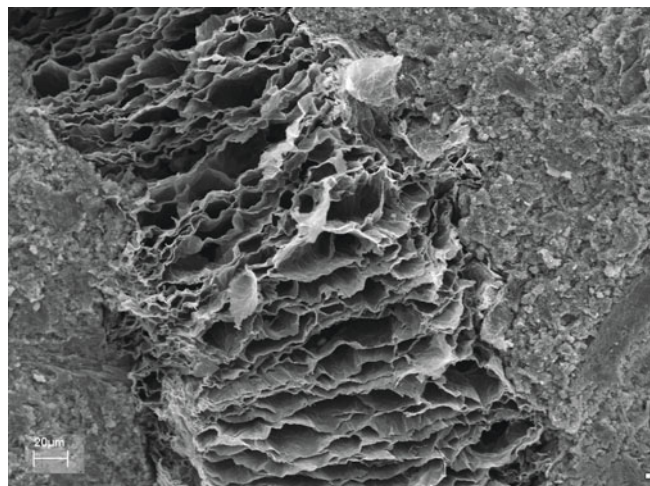


Figure 5. SEM spectrum for cement composites with EG covered by the oligomer film

CONCLUSION

EG/oligomer coming from the electro-oxidation of phenol, useless from the electrochemical point of view, was used as component of polymer-cement mortar. It was shown that EG covered by the oligomer film can be implemented in cement mortars giving the improvement of flexural parameters, especially flexural toughness of the composite. Oligomer film formed on EG surface made graphite flakes more durable and resistant to bending, and moreover, due to the interaction with polymer network led to the improvement of flexural toughness of polymer-cement mortar.

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