Electrochemical synthesis of multilayer graphene oxide and its application in composite materials

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Abstract. An electrochemical method for multilayer graphene oxide production by anodic oxidation of graphite dispersed in sulfuric acid is proposed. The possibility of sequential dispersion of graphite during the electrochemical oxidation and hydrolysis is shown. It was established that the carbon nanostructured materials obtained are prone to agglomeration in aqueous dispersions. After sonication, the particle size of the oxidized graphite was found to significantly decrease with the formation of the multilayer graphene oxide. It was elucidated that the structure of the obtained material consists of multigraphene planes with a thickness of 0.01-0.10 µm, and the pore size is 1-10 µm. The possibility of using the graphene oxide to produce polymer composite materials and composite electrochemical coatings is considered. Regarding the kinetics of the epoxy composition curing, it was observed that the graphene oxide affects the structure formation, which was indicated by an increase in the gel formation duration from 45 to 64 min and curing from 53 to 78 min, with an increase in the maximum curing temperature from 105 to 116 °C. Through the method of thermogravimetric analysis, it was established that the introduction of the graphene oxide reduces the thermal stability of the epoxy composites, but provides increased Vica heat resistance from 100 to 125-158 °C. The width of the passive state area for the nickel-graphene oxide composite electrochemical coating was found to be 1.32-1.40 times higher than that for the pristine nickel coating.

1. Introduction

Graphene possesses unique properties, which makes it possible to use for developing supercapacitors [1], superconductors and nanosensors [2-4], composite materials and coatings [5,6]. Currently, applied research employs single- and multilayer graphene materials obtained from graphite oxide, which is mainly synthesized through the Hummers method [7-10]. However, the production of graphite-intercalated compounds and multilayer graphene oxide (GO) is also possible using the electrochemical method in sulfuric or nitric acids [11,12].

Modification of polymers by carbon functional additives (graphite, carbon nanotubes, thermally expanded graphite, fullerene C₆₀, or multilayer graphene) have been widely studied to produce polymer materials with a given set of functional and consumer characteristics [13-15]. Despite the large number of works devoted to the investigation of the effect of various carbon modifiers, at present, there is still no complete information on issues related to studying that effect on the structure formation and the structural and operational characteristics of polymer composite materials.
After co-deposition of metals with particles dispersed from electrolyte suspensions, composite electrochemical coatings (CECs) are formed [6,16]. The functional properties of such coatings are largely determined by the dispersed phase nature. Previous studies have shown that the inclusion of graphite electrochemical oxidation products in the matrix of electroplated coatings leads to an improvement in their tribological and corrosion properties [16]. In this regard, electrochemically synthesized GO appears to be a promising dispersed material for improving the operational characteristics of composite coatings.

Considering the aforementioned, the aim of this work was to study the electrochemical synthesis and structure of multilayer GO, as well as the functional properties of composite materials and coatings modified by it.

2. Materials and methods

Dispersed graphite powders (Standard GB/T 3518-95, Sunshine Resources Holdings Limited, Beijing, China) with a particle size ranging from 160 to 200 µm were employed in the present research. 83-% H₂SO₄ was used as electrolyte. Electrochemical measurements were carried out with an IPC Pro MF potentiostat (Volta, St.-Petersburg, Russia) in a three-electrode cell using a platinum cathode and platinum current wire. A mercury sulfate electrode (MSE) (CHI150, MIRONG, Shanghai, China) was used as a reference electrode. The synthesized compounds were hydrolyzed with subsequent drying at 90-100 °C. Studies on the particle size distribution of oxidized graphite in aqueous suspensions were carried out by an Analysette-22 NanoTec laser analyzer (Fritsch, Idar-Oberstein, Germany). The surface and structure of nanostructured graphite particles were studied using a EXplorer Aspex scanning electron microscope with built-in energy dispersion analysis (Aspex Corporation, Sheffield Drive, Delmont, USA). FTIR spectroscopy of the nanostructured graphite particles was performed on an IRTracer-100 instrument (Shimadzu, Tokyo, Japan). X-ray phase analysis was carried out on an ARL X'TRA X-ray diffractometer (Thermo Fisher Scientific SARL, Ecublens, Switzerland).

To study the possibility of using electrochemically synthesized multilayer GO as a polymer matrix, the previously developed epoxy composition [5], consisting of epoxy resin (ED-20) – 100 mass parts (m.p.), trichloroethyl phosphate (TCEP) – 40 m.p. and polyethylene polyamine (PEPA) as hardener – 15 m.p., was used as CEC. 0.01-0.50 m.p. of the GO were introduced into this epoxy composition. To increase the uniformity of distribution of the GO, its activation and the activation of the binder surface, the composition was sonicated. The parameters of ultrasonic exposure for the dispersed and filled CECs were chosen from our previous paper [17,18]: ultrasound frequency - 22±2 kHz, and duration – 60 min.

Studies on the CECs were carried out as follows: determination of bending stress and modulus of elasticity in bending [according to ISO 178:2010], determination of tensile strength and modulus of elasticity [according to ISO 527-2:2012], determination of compressive strength [according to ISO 604:2002], determination of impact strength [according to ISO 179-1:2010], Brinell hardness test [according to ISO 2039-1:2001], and determination of Vica heat resistance [according to ISO 306:2004]. Changes in mass, their rate and values of thermal effects during sample heating were investigated through the method of thermogravimetric analysis using a Paulik-Paulik-Erdei Q-1500D derivatograph system (MOM, Budapest, Hungary) under the following experimental conditions: sample weight – 100 mg, environment – air, heating interval – to 1000 °C, heating rate – 10 °C/min, and relative error – ≤ 1 %. Thermal conductivity and thermal resistance was determined an ITP-MG4 100 device (Stroypribor, Chelyabinsk, Russia) according to ISO 22007-2: 2015.

For electrochemical studies, the CECs were deposited in electrolytes – NiSO₄·7H₂O (220 g/L), NiCl₂·6H₂O (40 g/L); CH₃COONa (30 g/L) and graphene oxide (10 g/L) – on a steel base (steel 45) at 25 °C, with the electrolytes being mixed. Electrolytic coatings of pure nickel were obtained from this electrolyte without a dispersed phase. Corrosion tests of the nickel coatings were carried out by recording anode potentiodynamic curves in a 3-% NaCl solution at potential sweep rate Vₚ = 10 mV/s. The curves were recorded before a sharp rise in current. The corrosion resistance of the coatings was judged by the length of the passive state potential area.
3. Results and discussion

3.1. Analysis of oxidized graphite
The electrochemical oxidation was performed in the galvanostatic mode at a current of 400 mA (200 mA/g graphite) with a transmission of electric capacity of 700-1500 mA h/g and potential control. The increase in the volume of the suspension graphite electrode recorded during the anodic oxidation of the graphite was found to be 180-200 % of the original volume. During the electrochemical oxidation of natural graphite, the carbon matrix undergoes changes accompanied by an increase in interlayer distances from 3.34 Å (in the pristine graphite) to 7.78 Å (in the oxidized graphite). This can be explained by the formation of intercalated graphite compounds, as well as the formation of oxygen-containing surface functional groups [9,19-21]. Like in the case of GO synthesized through the Hummers method [9,10], the surface functional groups mainly consist of hydroxyl and phenolic [the peak at 3417 cm⁻¹] and hydroxyl groups between graphene layers [the band between 2800 and 3100 cm⁻¹] (figure 1); the presence of these groups indicates the formation of GO. The sp² hybridization of C=C in the graphene structure is confirmed by a peak at 1627 cm⁻¹ [9]. The peak at ~2300 cm⁻¹ corresponds to absorbed CO₂ molecules [10]. The band between 1106 and 1005 cm⁻¹ corresponds to C-O-C (epoxy groups) [10]. The band at 1384 cm⁻¹ represents a deformation oscillation in -COOH-groups. As a result of hydrolysis, exfoliation of oxidized graphite particles occurs, resulting in a 10-11-fold increase in the volume.

The distribution range of the oxidized graphite particles in the aqueous suspension is greatly expanded (0.2-1800 µm, modal size 355 µm) (figure 2). The particles are prone to agglomeration, which requires mechanical or ultrasonic action, after which the particle size distribution range becomes equal to 0.2-400 µm, with a modal size of 91 µm.

Figure 1. FTIR spectra recorded for the electrochemically oxidized graphite.
Figure 2. Particle size distribution for the oxidized graphite. 1,1' – integral, 2,2’ – differential; 1',2' – when exposed to ultrasound (50 W). \(dQ_3(x)\) [%] - distribution density; \(Q_3(x)\) [%] - cumulative distribution; and \(x[\mu m]\) - particle size.

The structure of the oxidized graphite particles represents a sequence of ordered layers, the thickness of individual layers may be < 0.1 \(\mu\)m (figure 3), which can also be noted for the oxidized graphite obtained through the Hummers method [9,10]. The radiograph records the peak characteristic of GO at \(2\theta = 11.45^\circ\) (figure 4), which corresponds to the interlayer distance of 7.78 Å and allows to classify the resulting compound as multilayer GO [3,19,20].

Figure 3. SEM images of the electrochemically oxidized graphite. Electric capacity: 700 (a), 900 (b) and 1500 (c) mA h/g.
3.2. Studies of composite materials

From the results obtained on the epoxy composites presented in Table 1, it can be seen that the optimum GO content is 0.1 m.p., since at this level, the maximum values of physical and mechanical properties were achieved. Relative to the CEC without GO, the parameters of the CEC containing the 0.1 m.p. GO were increased 2.3-fold (bending failure stress and bending elastic modulus), by 57 % (compressive strength), 77 % (tensile strength), 55 % (tensile elastic modulus), 75 % (impact strength), and 50 % (hardness).

Table 1. Properties of the epoxy compositions developed.

| Composition (m.p.) + PEPA (15 m.p.) | $\sigma_b$, MPa | $E_b$, MPa | $\sigma_c$, MPa | $E_t$, MPa | $a_{imp}$, kJ m$^{-2}$ | $H_b$, MPa |
|------------------------------------|----------------|------------|----------------|------------|-------------------|------------|
| ED-20 (100) + TCEP (40)            | 53            | 1750       | 70             | 36         | 1610              | 8          |
| ED-20 (100) + TCEP (40) + GO (0.05)| 109           | 3400       | 101            | 56         | 2114              | 8          |
| ED-20 (100) + TCEP (40) + GO (0.1)| 120           | 4086       | 110            | 64         | 2509              | 14         |
| ED-20 (100) + TCEP (40) + GO (0.5)| 93            | 4282       | 114            | 54         | 2785              | 10         |

$\sigma_b$ – bending failure stress; $E_b$ – bending elastic modulus; $\sigma_c$ – compression strength; $\sigma_t$ – tensile strength; $E_t$ – tensile elastic modulus; $a_{imp}$ – impact strength; $H_b$ – Brinell hardness; coefficient of variation in properties – 4-7 %.

Regarding the kinetics of the epoxy composition curing, it was observed that the GO affects the structure formation, which is indicated by an increase in the gel formation duration from 45 to 64 min and curing from 53 to 78 min, with an increase in the maximum curing temperature from 105 to 116 °C. Through the method of thermogravimetric analysis, it was established that the introduction of the GO reduces the thermal stability of the epoxy composites (figure 5) but provides increased Vica heat resistance from 100 to 125-158 °C.
Figure 5. Data of the thermogravimetric (TG – mass loss, %) analysis of the samples:
1 – ED-20 (100 m.p.) + TCEP (40 m.p.) + PEPA (15 m.p.);
2 – ED-20 (100 m.p.) + TCEP (40 m.p.) + GO (0.1 m.p.) + PEPA (15 m.p.);
3 – ED-20 (100 m.p.) + TCEP (40 m.p.) + GO (1.0 m.p.) + PEPA (15 m.p.).

Due to the fact that the GO has a sufficiently high heat conductivity, the introduction of even its small amounts into the epoxy composition increases the thermal conductivity coefficient by 2.6-3.0 times, and decreases the thermal resistance (Table 2).

Table 2. The GO effect on the thermal conductivity of the epoxy compositions.

| Composition (m.p.) + PEPA (15 m.p.) | Heat conductivity coefficient, W (m K)^{-1} | Thermal resistance, m^2 K W^{-1} |
|----------------------------------|------------------------------------------|---------------------------------|
| ED-20 (100) + TCEP (40)          | 0.105±0.0058                             | 0.086±0.0043                    |
| ED-20 (100) + TCEP (40) + GO (0.1) | 0.274±0.0090                             | 0.036±0.0015                    |
| ED-20 (100) + TCEP (40) + GO (0.5) | 0.322±0.0098                             | 0.030±0.0012                    |

The comparison between the optimum CEC developed (GO content – 0.1 m.p.) and the existing analogs showed its competitiveness, as it possesses comparable and even higher (regarding some parameters) physical and mechanical characteristics (Table 3).

Table 3. Comparison between the developed epoxy compositions and analogs.

| Composition (m.p.) | σ_b, MPa | E_b, MPa | σ_t, MPa | E_t, MPa | a_{imp}, kJ m^{-2} | H_v, MPa |
|--------------------|----------|----------|----------|----------|-------------------|----------|
| ED-20 (100) + TCEP (40) + GO (0.1) + PEPA (15) | 120 | 4086 | 64 | 2509 | 14 | 126 |
| Analogs            |          |         |         |         |                  |          |
| ED-20 (100) + Fullerene C_{60} (0.1) + PEPA (10) [4] | 75 | 3100 | - | - | 9 | - |
| ED-20 (100) + TCEP (42) + WPPT (0.1) + PEPA (15) [7] | 97 | 2614 | 52 | 2095 | 14 | 120 |
| ED-20 (100) + TCEP (40) +MTW (20) + PEPA (15) [6] | 53 | - | - | - | 7 | 110 |

WPPT – whiskers of potassium polytitanates, MTW – millet threshing waste heat-treated at 350 °C.
The electrochemical studies showed that in the presence of the GO, nickel is deposited at less negative potential values (figure 6). During the electrodeposition, in the case of the nickel-GO CEC coating, the current increases compared to the nickel coating without dispersed phase, thereby indicating an increase in the cathode process rate.

**Figure 6.** Potentiodynamic polarization curves of the nickel deposition without additive (1) and (2) together with the GO.

**Table 4.** The width of the passive state area $E, V$ of nickel-based coatings obtained at different cathode current densities $i_C$.

| $i_C$, A/dm$^2$ | 6  | 7  | 8  | 9  | 10 |
|-----------------|----|----|----|----|----|
| Nickel          | 0.60 | 0.62 | 0.66 | 0.68 | 0.68 |
| Nickel-GO CEC   | 0.80 | 0.82 | 0.90 | 0.94 | 0.96 |

The introduction of dispersed GO particles into the nickel matrix leads to its structural changes, which, in turn, should affect the operational properties of electrolytic coatings. Corrosion resistance is of great practical interest. The studies on the nickel coatings in a 3-% NaCl solution showed that the width of the passive state area for the nickel-GO CEC is 1.32-1.40 times higher than that for the nickel coatings without dispersed phase (Table 4). This effect is due to several reasons. The CEC is more resistant to corrosion the higher area of its surface overlap by particles of dispersed phase because it provides a uniform distribution of corrosion current between the sites that prevent its spreading. When the GO particles are introduced into the nickel matrix, the pores become overlapped. Furthermore, in the composite coatings, the dispersed phase effect on the corrosion is revealed only in the case of formation of particles at phase boundaries or throughout the bulk of compounds more corrosion-resistant than the metal matrix. Otherwise, the occurrence of the corrosion process will not stop but will bypass the particles. Obviously, in the case of the nickel-GO CEC, such compounds are formed.

**4. Conclusion**

The possibility of obtaining multilayer GO through electrochemical oxidation of natural graphite powder dispersed in H$_2$SO$_4$ was shown. It was established that the graphite is consistently exfoliated
during anodic oxidation with the formation of graphite oxide and subsequent hydrolysis with the formation of multilayer multigraphene. In comparison with the conventional Hummers method, the main advantage of the technique herein proposed is that the strong oxidizers (KMnO₄, K₂Cr₂O₇, etc) are not used, thereby increasing the environmental safety of the process and the purity of the compounds synthesized.

The possibility of directed control over the performance properties of epoxy composites through using small amounts of finely dispersed multi-layer GO was demonstrated. This provides the development of epoxy composites with high performance properties that meet the requirements of most industries. Thus, these materials can be used for sealing electronic products, as well as for impregnating and filling components in the aviation, shipbuilding and automotive industries.

Besides, it was shown that the introduction of the GO dispersion into the nickel electrolyte facilitates the process of electrodeposition and contributes to the formation of composite coatings. It was found that the GO particles increase the width of the passive state area by 1.32-1.40 times.

Thus, GO-containing CECs can be used as corrosion-resistant materials in machine building and the other industries.

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