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Chemistry

EMI Absorber Materials Based on Graphene/Polymer Composites

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(Presented by Academy Member Shota Samsoniya)

A growing demand for electronic and communication devices in various spheres of industry has given rise to a new challenge, known as electromagnetic pollution. The electromagnetic (EM) radiation caused pollution is so serious that the WHO has included this problem in a number of the most harmful problems for human health. Correspondingly, the development and manufacture of novel electromagnetic interference (EMI) radiation shielding materials has become rather urgent. An ideal EMI shielding material should be light, thin and characterized by a high EMI absorption degree, a broad absorption band and multi-functionality. Polymers offer several advantages over traditional metals and ceramics used for EMI shielding. They can be easily shaped into a wide variety of morphologies and are substantially lighter. Graphene structures containing polymer (Acrylnitrilbutadien styrol and Polydimethylsiloxane) nanocomposites is developed for application as EMI shielding material. The reflection coefficients of the produced absorbing materials were measured in the frequency range from 10 KHz to 6 GHz. The reflection measurements were performed by ASTM D4935 (Standard test methods for measuring the electromagnetic shielding effectiveness of planar materials) method. The structure and composition of the obtained materials were studied by UV, XRD, Raman and SEM. Obtained polymer nanocomposites have potential to use as EMI shielding material. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Graphene, polymer, nanocomposite, electromagnetic, shielding

Recently electromagnetic radiation has been considered a danger to electronics, biological systems, high quality information and safety technologies, etc., for when the electromagnetic waves interfere with a signal coming from an electronic device, a noise known as the electromagnetic interference pollution (EMI) occurs. In general, EMI pollution may be considered as an unwanted action in modern engineering that can lead to a serious human health disorder, such, for example, as a headache, sleeping disorders, trepidation etc. The EMI affects the life and performance of electronic devices used in communication facilities (cell phones, computers, etc.), electronic appliances (microwave ovens, etc.,) and in the automobile industry (integrated electronic systems, etc.). Thus, such kind of pollution has become a global challenge and its reduction is achievable only by making the electric radiation shielding materials. The EMI shielding/protective shell is determined by its radiation absorptive/reflective capacity, which serves as a barrier to radiation leakage into a material. Generally, conducting materials are used as the EMI shield, such, for example, as metals, although they are characterized of less flexibility, more weight and high prices. Therefore, the active work on the production of such new polymeric composites that could compete with the above-mentioned materials is under way [1-3].

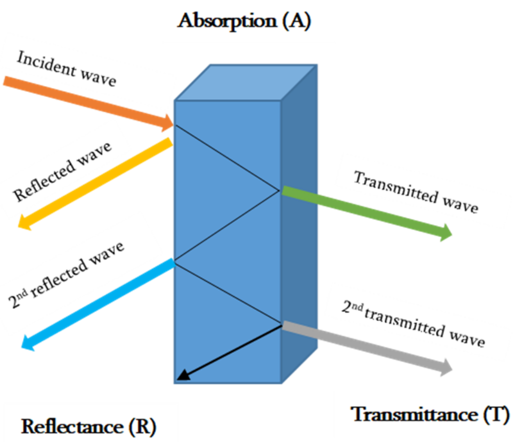

Fig. 1. Schematic diagram of incident, reflected and transmitted power and electro-magnetic field intensities when an EM wave is incident on a 3D material.

After discovery of the unique properties of graphene, new possibilities for research and development of polymer nanocomposites have been opened up. The sphere of application of the innovative polymer nanocomposites produced by using other graphene and carbon nanostructures is enormous, since such nanocomposites can be characterized by extraordinary multifunctional properties [4-6], which further increases the number of products applied in innovative technologies. Based on the composition and processing complexity, a serious question for mass production of such nanocomposites is how control over the structure, dispersion degree, and morphology will be exercised, so that a material with best properties is produced.

The shielding efficiency in terms of refection/absorption (SE_T) Shielding efficiency (SE_T) could be defend as parameter that measures how well a material impedes the EM energy of a certain frequency when passing through it. Fig. 1 represents the possible interactions of EM waves with materials.

When the EM waves fall on the front-face of the material then a certain part of the incident power (PI) is reflected (PR), while a certain part is absorbed and dissipated in form of energy, and the remaining part is transmitted (PT) through the shielding material. Therefore, three different processes namely refection, absorption and multiple internal reflections contribute to the whole attenuation, corresponding to shielding effectiveness SE_R, SE_A and SE_M, respectively (1).

$$SE_T = 10\log\frac{PI}{PT} = 20\log\frac{EI}{ET} = 20\log\frac{HI}{HT} = SE_R + SE_A + SE_M \quad (1)$$

Here P, E and H are the intensity of force, electric and magnetic fields, the radiation incident (I), reflection (R) and transmittance (T). When it concerns the shielding efficiency from EMI of the composite materials, this can be studied as their electroconductivity function, which, in turn, depends on the conductivity, morphology, and dispersive power of a filler, as well as the interaction between the filler's particles and the matrix molecules:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (2)$$

where σ is electroconductivit in c/cm, μ is magnetic conductivity of the material, which equals 1 for nonmagnetic materials and *f* is radiation frequency within the MHz limits (2) [4,5]:

Measuring technology. To fulfill the tasks an electromagnetic radiation protective device has been designed and manufactured. The device consists of two (52 mm diameter and 20 mm thick, with a 15 mm hole) disks, interconnected by 8 M4 screws; it is desirable that initially the whole "completed" duralumin cylinder be drilled with a 15 mm drill in the center, ensuring thus the complete registration of the centers with the hole diameter. Also desirable would be drilling of 8 3.5 mm holes for M4 screws and then 200 mm-thick disks would be cut. After cutting, the first disk holes will be widened up to 4 mm, while M4 screws will be cut in the second disk. 4 N connectors will be attached on both disks by the M3 screw. The disks 1 and 2 are made of duralumin or brass cylinders, D=55-60 mm.

Polymers. Polymers offer several advantages over traditional metals and ceramics used for EMI shielding. They can be easily shaped into a wide variety of morphologies and are substantially lighter. Conducting polymers are used in different fields: in sensors, to protect metals from corrosion, in energy storage devices, etc. The character of conducting polymers depends on their doping degree, dopant ion sizes, water content, etc. In spite of the fact that conducting polymers possess a whole number of advantages, they still are not sufficiently flexible and processable in the case of mass production [7,8]. Therefore, there are frequents cases of using non-conducting polymers and of adding dopants into them, because such polymers are cheap and accessiible, less time-consuming and enfironmentally-friendly. In addition, they allow for their mass production. In order to improve the electric and thermal conductivity and mechanial properties, a polymer is added with metals or carbon nanostructures. There are several methods of filler doping in the polymer matrix: solution mixing, melt mixing and the *in situ* polymerization. Upon using the solutions mixing method, the polymer and the filler are solved in the same solvent, then mixed together, removed from the solvent and dried. The *in situ* polymerization is applied where the polymer is insoluble and thermally unstable.

Experimental

Synthesis of graphene oxide (RGO). Synthesis of graphene oxide have conducted by intercalation method from graphite. Graphite flakes (2 g) mixed in 50 mL of H_2SO_4 (98%) and potassium permanganate (6 g) very slowly during 1 h. The flask kept under at ice bath (27-35°C) with continuous stirring. After 1 h 100 ml water was added in the mixture. Then continue stirring again about 1 h and 20 mL H_2O_2 was added. After washing and filtration, the mixture centrifugation has done. Stable graphene oxide suspensions have obtained which used as reinforcement materials in ceramic composite (Fig. 2).

Synthesis of reduced graphene oxide. The obtained GO was mixed with 100 mL of water and

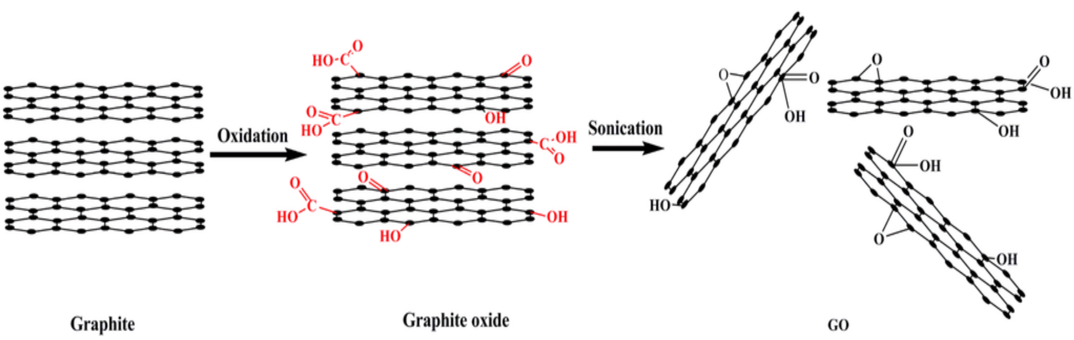

Fig. 2. Scheme of the preparation of GO.

sonicated for 1 h using an ultrasound homogenizer. Obtained suspension was carried out in microwave and collected reduced graphene oxide powder.

Preparation of polymer nanocomposites. Polymer nanocomposites were obtained by mixing the calculated amounts of Polydimethylsiloxane (PDMS) and Acrylnitril-butadien-styrol (ABS) dissolved in chloroform (5wt.%) and reduced graphene oxide. The mixture was evaporated and dried. Then obtained solid composites were pressed.

The structure of the obtained graphene oxide, reduced graphene oxide and polymer nanocomposites were characterized by XRD (Diffractometer DRON-3M), Ultraviolet–visible "DRAWELL" DU-8600R, Electronic microscope, Raman spectra were registered with a Raman microscope Nanofinder High End (Tokyo Instruments). The reflection measurements were performed by ASTM D4935 (Standard test methods for measuring the electromagnetic shielding effectiveness of planar materials) method. All measurements were conducted at room temperature.

Results and Discussion

Graphene is a single atomic layer of sp^2 carbon atoms. Few- and single- layer transferable graphene nanosheets were first obtained by mechanical exfoliation ("Scotch-tape" method) of bulk graphite [9-10]. Graphene has unique physical-chemical properties. Today graphene and it's derivatives (graphene oxide, reduced graphene oxide and etc.) are widely used for preparation of graphene/composites.

Graphene oxide, obtained by oxidation of graphite contains oxygen functional groups (-COOH, -OH, -O-O-, -CHO), after reduction of it, reduced graphene oxide (rGO) is received, in which C:O ratio increases due to partial removal oxygen atoms (deoxygenation). Many methods are used for obtaining of reduced graphene oxide such as, using organic and inorganic compounds as reducers; treatment of graphene oxide suspensions by ultrasound homogenizer and microwave. Interest in GO increased dramatically after graphene, a single layer of graphite, was first isolated.

The properties of graphene-polymer based composites depend on filler distribution, ratio of filler to polymer, the type of polymer matrix, and filler and matrix bonding. In our research we have synthesized RGO and mixed into matrix.

For purpose, Graphene based polymer (PDMS and ABS) nanocomposites were synthesized. Scanning Electron microscopy was used to study the morphology and structure of materials. SEM images shows that nanocomposites reveal the porous structures.

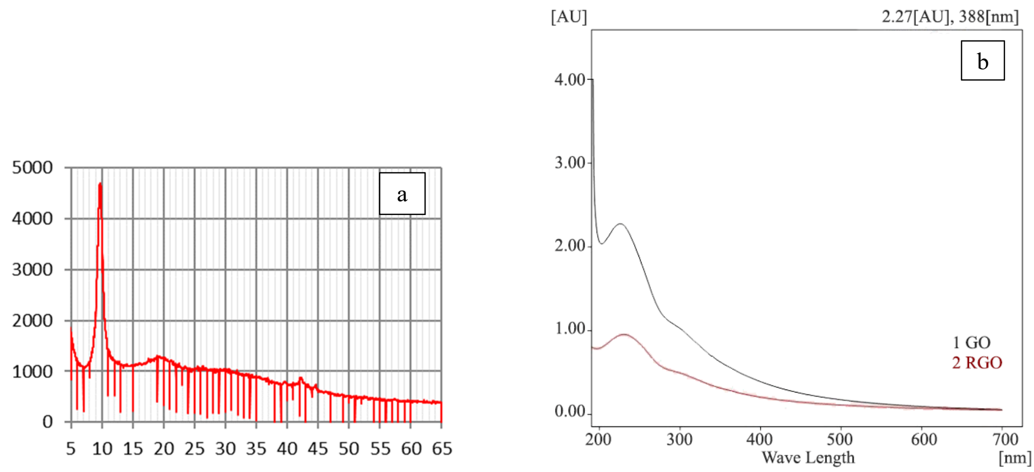

Fig. 3. XRD (a) and raman (b) spectra of GO.

RGO structure was investigated by XRD method, this is the most widely used technique for general crystalline material characterization. Characteristic diffraction peak at 10º was observed for graphene oxide (Fig. 3a). The Raman spectrum of Graphene oxide observed D mode at $\approx 1350\,cm^{-1}$ and G mode at $\approx 1600\,cm^{-1}$ corresponding to common-mode lattice vibrations. The intensity of G mode is higher than that of D mode for GO.

In the UV-Vis spectra (Fig. 3b), the main peak at 230 nm and the shoulder peak at 300 nm stand for π-π^* transitions of C=C bond from graphitic carbon of GO and n-π^* transitions of C=O bond from oxidized carbon of GO respectively. Ultrasound homogenizer method of reduction has a fundamental role in the synthesis of GO sheets, because it is relatively simple and cost-effective compared to classical methods. The GO can be well dispersed in water by sonication due to the hydrophilic nature of its graphene layers. The obtained suspension was mixed with magnetic stirring and then treated by microwave.

The reflection measurements were performed by ASTM D4935 for graphene based PDMS/ABS nanocomposites. Materials were measured in the frequency range from 10 KHz to 6 GHz. We can note that materials can absorption ability in the ≈4.5 – 5 MHz area.

Conclusion

This work has developed a method of reduced graphene oxide production, where the reduction was achieved using ultrasonic waves. The materials identification and structural-morphological characterization were undertaken using XRD, UV, Raman and SEM. The reflection measurements carried out by ASTM D4935 method. The graphene-based nanocomposites developed in this study have a potential to use as EMI shielding material.

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ქიმია

ემგ მშთანთქმელი მასალები გრაფენი/პოლიმერული კომპოზიტების ბაზაზე

ნ. ჯალაღონია*, თ. კუჭუხიძე*, ნ. დარახველიძე*, ლ. კალატოზიშვილი*, ე. სანაია*, გ. ბოკუჩავა*, ზ. ხვიტია*

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ბოლო ათწლეულში თანამედროვე მსოფლიოს ელექტრონული და საკომუნიკაციო მოწყობილობების მზარდმა მოთხოვნილებამ მრეწველობის სხვადასხვა სფეროში წარმოშვა ახალი გამოწვევა, რასაც ელექტრომაგნიტური გამოსხივებით დაბინძურებას უწოდებენ. უნდა აღინიშნოს, რომ ელექტრომაგნიტური (ემ) გამოსხივებით დაბინძურება იმდენად არსებითი და საყოველთაო მნიშვნელობის საკითხია, რომ ჯანდაცვის მსოფლიო ორგანიზაციამ ეს პრობლემა შეიტანა ადამიანისათვის ყველაზე საშიშ პრობლემათა სიაში. ამის შესაბამისად, უნდა აღინიშნოს, რომ ძალზედ აქტუალური და მნიშვნელოვანი ხდება ელექტრომაგნიტური გამოსხივებისაგან დამცავი ახალი მასალებისა და ბარიერების შექმნა. ემგ-ს მშთანთქმელი იდეალური მასალა აუცილებლად უნდა აკმაყოფილებდეს შემდეგ მოთხოვნებს: იყოს მსუბუქი, სისქით თხელი, ამასთან უნდა ხასიათდებოდეს მაღალი ემგ-ს აბსორბციის უნარით, შთანთქმის სიხშირის ფართო დიაპაზონით და მრავალფუნქციური თვისებებით. დღესდღეობით ემგ-გან დამცავ მასალებში გამოყენებულ მეტალებსა და კერამიკებთან შედარებით პოლიმერებს გააჩნია მთელი რიგი უპირატესობანი - მათ აქვთ უნარი ადვილად იცვალონ ფორმა და, ამასთან, წარმოადგენდნენ არსებითად მსუბუქ მასალებს. ამ მიზნით, გრაფენის სტრუქტურების შემცველი პოლიმერული (აკრილო ნიტრილ ბუტადიენ სტიროლი და პოლი დიმეთილ სილოქსანი) ნანოკომპოზიტები სულ უფრო აქტიურად იქნა გამოყენებული და განვითარებული ემგ-გან დამცავ მასალებში ჩასართავად. მიღებული ექსპერიმენტული მასალებისათვის არეკვლის კოეფიციენტი განსაზღვრულ იქნა 10კჰ-დან 6გჰ-ის დიაპაზონში. არეკვლის გაზომვა განხორციელდა ASTM D4935 მეთოდით (ელექტრომაგნიტური გამოსხივებისაგან დამცავი ეფექტურობის განსაზღვრის სტანდარტული მეთოდი გეგმიური მასალებისათვის). მიღებული კვლევითი მასალების სტრუქტურა და შედგენილობა შესწავლილ იქნა ულტრაიისფერი სპექტროსკოპით, რენტგენოსტრუქტურული ანალიზით, რამან სპექტროსკოპიით და ელექტრონული მიკროსკოპით. მიღებულ პოლიმერულ ნანოკომპოზიტებს გააჩნიათ პოტენციალი გამოყენებულ იქნან როგორც ემგ-გან დამცავი გარსის მასალები.

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