ELECTROMAGNETIC SHIELDING ABILITY OF BALL-MILLED POROUS CARBON-REINFORCED COMMERCIAL PAINTS

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ABSTRACT

Carbon materials have been attracting intensive attention especially after the discoveries of fullerenes in 1985 and graphene in 2004. Our aim is to develop an efficient, low-cost and large-scale synthesis method of a carbon material called porous carbon, which is a collection of nanoscale mono- and multi-layer graphene flakes. This work presents the method of producing porous carbon and the capability of electromagnetic shielding of a typical commercial paint reinforced by the fabricated carbon material.

Keywords: electromagnetic shielding, porous carbon, ball milling.

1. INTRODUCTION

Passengers who travel by airplanes are familiar with the demand of the pilots that all portable electronic devices such as mobile phones and laptops, must be turned off just before taking-off and landing for the reason of safety. However, it seems to be not so clear for most people about the cause of such a demand. The truth is that all electronic devices are sources of electromagnetic radiation so that if there is an occurrence of electromagnetic interference (EMI), the operation of some equipment of the planes may be disturbed and therefore may create severe risks. According to Vasquez *et al.* (see Ref. [1] and references therein) there were already expensive lessons in the aviation. Typically they were the five crashes of Blackhawk helicopters in the United States shortly after their introduction into service in the late 1980s with the cause being found to be EMI occurring in the electronic flight control system due to very strong radar and radio transmitters [2], and the accidents of the Trans World Airline flight 800 [3] and Harrier Jump Jet wherein the pilot emergency ejector seat was determined to be triggered [4] by EMI. Besides, in the aviation, pilots usually meet anomalies with their navigation equipment that their causes are also determined to be EMI generated by the use of personal electronics in the airplane [5]. In daily life, the behaviors of EMI are also very common such as disturbances in television reception and/or mobile communication equipment. Even though the electromagnetic fields bring us lots of advantages in modern life, they sometimes are unseen enemies not only for electronic devices, but also for human life wherein the interference could disturb or jam sensitive components, destroy electric circuits, thus, it may prompt explosions and accidents [1].

Besides the introduction of criteria for designing electronic devices and exploring electromagnetic frequency bands, the development of advanced materials, which is capable of preventing or at least reducing the impact of EMI, is neccessary. Metals such as nickel and copper have been known for long time as the most common materials used for EMI shielding purpose due to their electric conduction ability. If metallic sheets were usually used to make Faraday cages in the past, metals in the forms of powder and fiber are becoming increasingly popular for the aim of reinforcing plastics and polymer composites. Recently, nano-reinforced polymer composites (NRPCs) have been attracting intensive consideration in developing [6 - 8]. However, according to Vasquez *et al* [1], typical limitations of materials used for EMI shielding are usually associated with corrosion susceptibility, long processing times, high equipment cost for production, difficulty of material utilization to build articles with complicated geometries, limited service life when using conductive layers due to peeling and wear, and high reinforcement concentration. NRPCs, e.g. carbon nanofiber, carbon nanotube, and nanowire reinforced polymer matrices, seem to overcome some of these limitations because they are lightweight materials with desired flexibility, corrosion resistance, and suitable for mass production through conventional plastic manufacturing technologies such as extrusion and injection molding.

Recently, there is an increasing interest in graphene, a new two-dimensional allotrope of carbon, from both fundamental research and application due to its very attractive properties [9-11, 12]. Though it is only one-atomic thick hexagonal layer of graphite, graphene is stable and mechanically strong [10]. It is also known as a chemically inert and especially electrically conductive material. While wafer-size graphene sheets with extremely high quality are required in electronics, just micron- and nano-scale graphene flakes in large amount are needed for material technologies [13]. In this paper, we report on a carbon nano material which can be massively produced using a rather simple physical method, namely the high-energy ball milling one. We demonstrate that such a kind of fine carbon powder with the foam and/or porous structure can be obtained by milling coke coal. This carbon powder is essentially different from black carbon whose morphology is perfectly amorphous. The obtained carbon powder, called porous carbon (PC), actually is a mix of nanoscale mono- and multi-layer graphene flakes deformed due to milling. By reinforcing some kinds of plastics as well as composites by PC, we found a significant enhancement of electrical conductivity of these materials. Particularly, we show the ability of electromagnetic shielding of a typical commercial paint reinforced by the synthesized PC material. The paper is organized into 4 sections in which our method and experimental processes are presented in Sec. 2, results and discussions in Sec. 3, and finally some remarks and conclusion in Sec. 4.

2. METHOD AND EXPERIMENT

2.1. Fabrication of porous carbon

The mechanical ball milling method was used to obtain small-size graphite powders long time ago [14]. It was also effectively used to fabricate carbon precursors for growing nanotubes [15 - 18]. This method therefore is suitable for producing nano carbon used for composite materials. In our work, the carbon source was taken from a type of rich carbon coal which is the product of an appropriate heat-treatment process, the coke. Pieces of such coal (raw material) were then milled to obtain PC through two phases: (i) crude grinding, and (ii) fine high-energy milling. In the former the iron vessels and the balls of iron or of agate were used to grind the raw material in an appropriate period of time. In the latter, i.e., after crudely milled, coal powder was high-energy milled using a vertically rotating planetary satellite ball mill (Retsch MP 400/2 with tungsten carbide balls and vessels). The milling was implemented in an environment of either ethanol (wet milling) or nitrogen gas (dry milling). The crystalline structure of the fine powder obtained after a certain period of time (e.g., 10, 50, 80 hours) was analyzed (using Bruker D5005 with copper radiation of 1.5406 Å of wavelength for measuring X-ray diffraction patterns) to see the phase transition process due to the milling. The form and surface morphology of the high-energy ball milled carbon powder were also analyzed using transmission electron microscope (using JEOL JEM 1010).

2.2. Reinforcing paint by porous carbon

In order to check the potential of the obtained PC for EMI shielding application we mixed it with commercial paint by various percentages and then sprayed the paint on a glass substrate to obtain a paint layer with an appropriate thickness. The electric conduction properties of the resulted paint were measured using the QT Instruments CEAST and DM mod 01940. The shielding effectiveness of such a paint layer was then measured using the vector circuit analyzer HP 8720D in the radio frequency band of 8-12 GHz. In our work, the epoxy paint is used with or without a curing substance. PC and substance of curing with desired percentages of amount were mixed in the paint and continuously stirred for about 24 hours at ambient conditions.

3. RESULTS AND DISCUSSION

3.1. Natural features of ball-milled porous carbon

First of all, it is instructive to address the carbon material used as the raw one in our work. In Fig. 1(a) we show the images of several pieces of coke coal, a very rich carbon coal usually used for iron processing. This carbon material in fact is a collection of pieces of graphite with very high quality of crystalline structure. Indeed, the X-ray diffraction pattern of the material presented in Fig. 1(b) shows significantly only two very sharp peaks located at the Bragg diffraction angles 2θ of 26.5^o and 55^o. This result obviously indicates the typical hexagonal structure of graphite and it also suggests that our used carbon source is quite pure. To confirm this point, a chemical component analysis was carried out. The energy-dispersive X-ray (EDX) spectrum shows the percentage of carbon in our used coal greater than 99%.

It is now interesting to see the transformation of the morphology and structure of coal due to the ball milling. As shown by Chen *et al.* [15] the ball milling causes a structural phase transition due to the impact of balls. To investigate this process we use an amount of about 30 grams of carbon powder consisting of about 40 micron-sized carbon pieces, obtained after crude grinding, for the high-energy milling in a vertical satelline ball mill. By keeping track the X-ray diffraction (XRD) patterns of the carbon powder after a certain period of milling time we can see how the transition occurs. Fig. 2 displays three XRD patterns obtained after milling for 10 hours (top blue curve), 50 hours (middle red curve), and 80 hours (bottom black curve). These results reveal that the intensity of the peak at the diffraction angle of 26.5^o decreases with the increasing of the milling time while the one at 55^o totally disappears after 10 hours of milling. It therefore suggests that during the milling the coal pieces are broken into graphite flakes, which preferably orient along the (002) direction. This observation is similar to what reported in [15] and [19]. According to Ref. [15] although the hexagonal structure of graphite is still dominant after 10 hours of milling, this phase is robustly weakened after milling for 15 hours, and is replaced by the so-called turbostatic structure with the lattice spacings of $d(002) = 3.46$ Å and $d(100) = 2.10$ Å. Intuitionally, one can expect the amorphous structure after a long enough time of milling. This is true and the presence of the amorphous phase manifests as the asymmetrical form of the XRD pattern at the Bragg diffraction angle of 26.5^o as seen in the bottom black curve, i.e., after 80 hours of milling. However, it should be noticed that even if the amorphous phase is dominant, there are still nanocrystalline pieces as mono- and/or multi-layers of graphite flakes. In the XRD patterns there are other three sharp peaks (observed in three patterns) approximately at the diffraction angles of 31.36^o, 35.58^o and 48.27^o. Actually, they are characterisitics of tungsten carbide particles which appear due to the abrasion of the balls and of the vessels which was also confirmed by the observation of Chen *et al.* [15]. Such an abrasion makes the carbon powder dirty but this is not always bad because in some cases such particles can play as catalytic agents for growing carbon nanotubes, carbon spheres, and/or carbon onion structures if the producted carbon powder is properly annealed [16-19].

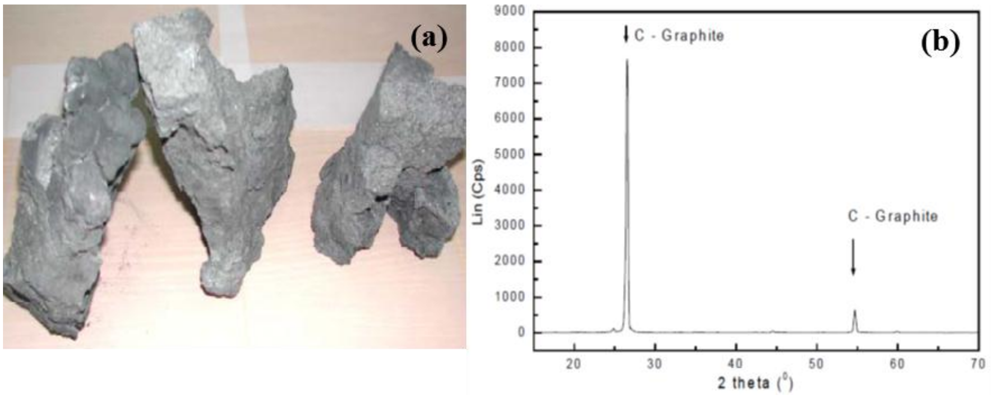

Figure 1. (Color online) Pieces of coal as used raw carbon material (a) and its X-ray diffraction pattern (b) showing the crystalline structure in the hexagonal graphite form.

In order to see the morphology of the ball-milled carbon powder the TEM images of a sample were then taken and analyzed. Figure 2 (right panel) is the TEM image of a sample of the carbon power obtained after 50 hours of ball milling. The image shows a foam structure with graphite flakes in the curved form as parts of small hollow spheres or dried leaves (look at the edges of the image). As suggested by Kang and Wang [20], such curved flakes consist of the hexagonal and pentagol carbon rings which play as the precursors for the growing of carbon nanotubes, onion spheres, etc, and thus they are deformed graphene nano sheets. Though characteristics of such a foam, or porous, structure were not quantitatively investigated in our studies, it is reasonable to recognize that the formation of this structure is essentially linked to the formation of the amorphous (disordered) phase wherein the micropores are presumably formed due to the agglomentation of carbon flakes under the impact of balls. Besides, the deformation of the flat graphene nano sheets into the curved ones is also an important agent contributing to the formation of the porous structure. Chen *et al.* [15] quantitatively investigated the formation of the porous structure of carbon powder by measuring the Brunaer-Emmett-Teller (BET) areas (defined as the sum of the internal and external surfaces) during the milling and showed that both the internal and external surfaces increase rapidly to a maximum value in the first periode of milling time of 15 hours, then decrease, and mostly saturate if continuously increasing the milling time. The increasing of the external surface is due to the fracture of carbon pieces under the impact of balls, while the increase of the internal one is due to the agglomeratation among carbon pieces. The saturation of the BET areas is the result of the compromise between the fracture and agglomeratation processes. In our work, carbon powders were just milled up to 80 hours but it is important to note that though there is a structural transition during the milling process, the final disordered phase is not completely amorphous but a mix of nanocrystalline graphite flakes and deformed graphene nano sheets. It is the presence of these contents that create the milled pourous carbon (PC) powders.

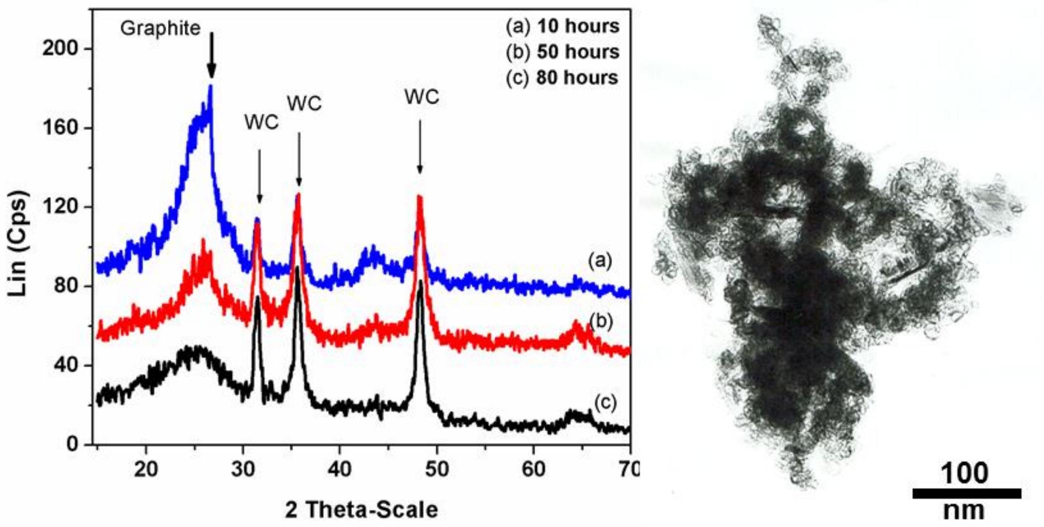

*Figure 2***.** (Color online) (a) X-ray diffraction patterns of carbon powder obtained by high-energy ball milling in nitrogen after different periods of time: 10 (blue), 50 (red), and 80 hours (black) and (b) Transmission Electron Microscopy (TEM) images of carbon powder obtained after 50 hours of ball milling in nitrogen environment showing a foam structure

3.2. Properties of PC-mixed epoxy paint

As analyzed in the previous subsection, by increasing the milling time (longer than 20 hours) the morphology of the resulted carbon powder becomes closer to that of the amorphous structure but, it is essentially different from that of black carbon. The resulted carbon powder is a mix of nanoscale carbon pieces wherein the presence of nanoscale curved graphite flakes (or deformed graphene nano sheets) is the most noticeable. Due to the outstanding properties of graphene-like strutures we then tried to use the obtained carbon product to reinforce epoxy and investigate some basic properties of the resulted paint. To this aim, we prepared five samples with different percentages of PC and labeled the samples as I_0, I_5, I_{10}, I_{20}, and I_{30} corresponding to 0 %, 5 %, 10 %, 20 % and 30 % of PC (fabricated in nitrogen gas environment). Table 1 lists the measured values of several quantities such as the dielectric constant and the volume resistance. As expected, the pure epoxy paint is an insulator so that its dielectric constant is the smallest and the resistance is the highest. Reinforcing this paint by PC makes it electrically conducting. Obviously, the higher the PC content, the lower the resistance and the higher the dielectric constant. Besides, several other qualities of the PC-reinforced paint, such as the chemical and solution durabilities, were also investigated (but not shown here, and will be discussed in details in a separated communication), indicating that all our samples are almost chemically inert.

Table 1. Several characteristics of PC-reinforced epoxy paint.

Sample	Dielectric constant	Volume resistance (Ω)
I_0	3.42	8.79×10^{14}
I_5	4.03×10^4	3.17×10^6
I_{10}	2.35×10^5	3.04×10^6
I_{20}	1.92×10^6	2.94×10^6
I_{30}	7.31×10^6	2.50×10^6

Since obtained paint samples are conductive we then became interested in its capability of shielding the electromagnetic interference. As defined, the ability of shielding of a material is quantified by the so-called shielding effectiveness (*SE*), which is measured in decibel (dB) as the logarith in base of 10 of the ratio of the incident (P_1) and transmitted (P_0) power,

$$SE = 10\log_{10}\left(\frac{P_1}{P_0}\right)$$

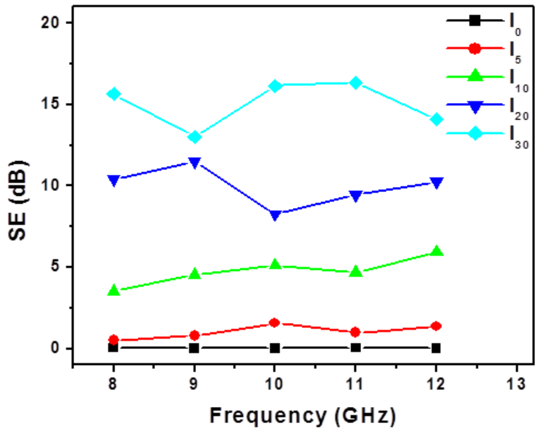

Figure 3. (Color online) Shielding effectiveness of various PC-reinforced epoxy paint layers as a function of frequency in the radio frequency range.

The shielding effectiveness of five samples of the PC-reinforced epoxy paint as a function of radio frequency is displayed in Fig. 3. According to [21], since our samples of the PC-reinforced paint have no magnetic property, i.e., with small magnetic permeability, the EMI shielding therefore takes place via the reflection mechanism. The results reveal that the shielding effectiveness is mostly a constant in the radio frequency domain ranging from 8 GHz to 12 GHz. The data also show that the higher the PC percentage, the higher the shielding effectivenss. The sample I_{30} with the highest percentage of PC has the largest SE as expected due to its lagest conductivity and dielectric constant. However, with the value of 16 dB, the shielding effectiveness of our samples is not too high. It is just haft of that of carbon fiber-reinforced polymer with 20 % carbon fibers which is reported in [21 - 23] to be 20 dB. In spite of that, our study was just a rough investigation of using PC massively produced by the ball milling method for the aim of the EMI shielding. It is understood that the value of SE depends on various parameters of material and therefore further studies on this interesting direction of research should be conducted.

4. CONCLUSIONS

In conclusion, we have reported results of developing a procedure of massively producing a carbon material which has very soft and porous structure starting from a very familiar crude type of coal. By analyzing the X-ray diffraction patterns and the TEM images of carbon powder during the ball milling we were able to realize a process of phase transition from the typical hexagonal graphite structure to the disordered, namely the turbostatic, one. Particularly, we pointed out that the disorded phase of final carbon powder does not completely similar to the amorphous one, but it is a mix of nanocrystalline carbon pieces such as graphite nano flakes, deformed graphene nano sheets, and even hexagonal and pentagol carbon rings, which are responsible for the formation of the pourous structure of the obtained carbon powder. Due to the very attractive properties of graphene-like structures we used the obtained porous carbon material to reinforce epoxy paint, a commonly commercial paint, and demonstrated that the resulted paint becomes electrically conductive with the dielectric constant and the conductivity increasing with the increase of the PC percentage. The durability of the PC-reinforced paint is quite good in various solutions, acid, and base. Particularly, the ability of the electromagnetic shielding of the PC-reinforced paint was also observed. The shielding effectiveness of the sample with 30% PC is 16 dB. Though this value is just moderate, it may suggest the interest of using pure graphene nano sheets in composites for the aim of the EMI shielding.

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REFERENCES

1. Vasquez H., Espinoza L., Lozano K., Foltz H., and Yang S. - Simple device for electromagnetic interference shielding effectiveness measurement *IEEE* (2009) 62-68
2. www/rvs.unibielefeld.de/publications/Incidents/DOCS/Research/Rvs/Article/EMI.html.
3. Scarry E. - The fall of TWA 800: The possibility of electromagnetic interference, The New York Review of Books (1998) 59.
4. http://www.glenair.com
5. Helfrick A. - Avionics and portable electronics: Trouble in the air?, Avionics News Magazine (1996).
6. Janda N. - Development of a predictive shielding effectiveness model for carbon fiber/nylon based composites, Master of Science Thesis, Chemical Engineering, Michigan Technological University (2003).
7. Glatkowski P., Mack P., Conroy J. L., Piche J. W., and Winsor P., US patent 6,265,466 (2001).
8. Nahass P. R., Friend S. O., and Hausslein R. W., US patent 5,651,922 (1997).
9. Barth A. and Marx W. - Graphene – A rising star in view of scientometrics, arXiv:0808.3320 (2008).
10. Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., and Firsov A. A. – Electric field effect in atomically thin carbon films, Science **306** (2004) 666-669.
11. Do V. N. and Pham T. H.- Graphene and its one-dimensional patterns: from basic properties towards applications, Adv. Nat. Sci.: Nanosci. Nanotechnol. **1** (2010) 033001.
12. Al-Saleh M. H, Saadeh W. H., Sundararaj U. – EMI shielding effectiveness of carbon based nanostructured polymeric materials: A comparative study, Carbon **60** (2013) 146–156.
13. Li D. and Kaner R. B. – Graphene-based materials, Science **320** (2008) 1170-1171.
14. Bacon G. E. – A note on rhombohedral modification of graphite, Acta Crystallogr. **3** (1950) 320-321, *ibi.* The reduction of the crystalline perfection of graphite by grinding **5** (1952) 392.

15. Chen Y., Fitzgerald J. D., Chadderton L. T., and Chaffron L. – Nanoporous carbon produced by ball milling, Appl. Phys. Lett. **74** (1999) 2782-2784.
16. Chen Y., Chadderton L. T., Fitzgerald J. D., and Williams J. S. A solid-state process for formation of boron nitride nanotubes, Appl. Phys. Lett. **74** (1999) 2960-2962.
17. Chen Y., Gerald J. F., Williams J. S., and Bulcock S. -Synthesis of boron nitride nanotubes at low temperatures using reactive ball milling Chem. Phys. Lett. **299** (1999) 260.
18. Chen Y., Conway M. J., and Fitzgerald J. D. - Carbon nanotubes formed in graphite after mechanical grinding and thermal annealing, Appl. Phys. A **76** (2**003**) 633-636.
19. Li J. L., Wang L. J., and Jiang W. - Carbon microspheres produced by high energy ball milling of graphite powder, Appl. Phys. A **83** (2006) 385-388.
20. Kang Z. C. and Wang Z. L. - On accretion of nanosize carbon spheres, J. Phys. Chem. **100 (1996)** 5163-5165.
21. Chung D. D. L. - Materials for electromagnetic shielding, J. Mater. Eng. Perform. **9** (2000) 350-354.
22. Li L. and Chung D. D. L.- Electrical and mechanical properties of electrically conductive polyethersulfone composites**,** Composites **25** (1994) 215.
23. Chung D. D. L. - Electromagnetic interference shielding effectiveness of carbon materials, Carbon **39** (2001) 279-285.

TÓM TẮT

KHẢ NĂNG CHẮN SÓNG ĐIỆN TỪ CỦA SƠN THƯƠNG MẠI ĐƯỢC GIA CƯỜNG BẰNG CACBON XỐP

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Vật liệu cacbon thu hút sự chú ý rất lớn của các nhà nghiên cứu, đặc biệt là sau phát hiện quả cầu fullerene vào năm 1985 và graphene vào năm 2004. Trong xu hướng đó, chúng tôi tập trung phát triển một phương pháp hiệu quả và có giá thành thấp để tổng hợp vật liệu cacbon xốp gồm các mảnh graphene đơn lớp và đa lớp. Trong bài báo này, bên cạnh việc trình bày phương pháp tổng hợp, chúng tôi khảo sát khả năng ứng dụng trong chắn sóng điện từ của sơn thương mại được gia cường bằng vật liệu cacbon xốp đó..

Từ khoá: chắn sóng điện từ, cacbon xốp, nghiền hành tinh.