MICROSTRUCTURES AND MECHANICAL PROPERTIES OF NANO-FLAKE GRAPHITE COMPOSITES

Wen-Shyong Kuo*, Tsung-Lin Wu, Hsin-Fang Lu** and Tzu-Sen Lo****
***Dept of Aerospace and Systems Engineering, Feng Chia Univ., Taichung, Taiwan**
****Graduate Inst. of Mechanical and Aeronautical Engg, Feng Chia Univ., Taichung, Taiwan**

Keywords: *Expanded Graphite, Nano-flake Graphite, Nano-composite, Mechanical Property*

Abstract

This paper studies the processing and mechanical properties of exfoliated graphite and the resulting composite. The natural graphite flakes were employed to make the exfoliated graphite through the intercalation of strong acids followed by a sudden heating at 1000 ℃. The thermal shock resulted in micro-explosion of the intercalated ions that leaded to the exfoliation of the graphene layers. The exfoliated graphite was further processed by a nano-dispersion method, and the separated nano-flake graphite was obtained. An epoxy resin was added to the dispersed nano-flakes, and a nano-composite was obtained. Some mechanical properties were studied, including thermal conductivity, impact, and compressive tests.

1 Introduction

This work studies the processing characteristics of nano-flake graphite composites. The nano-flakes were made from a *natural graphite* flake (NG), with an average of 80 mesh size the and a 95% carbon content (Fig.1). The flakes were chemically intercalated with a 98% surfuric acid and a 65% nitric acid solution at the room temperature. The intercalated compound was then subjected to a sudden heat within a 1000 ℃ oven for about 10 seconds, resulting in micro explosions within the graphite layers and forming the worm-like *expanded graphite or exfoliated graphite* (EG), as shown in Figs.2~3. Such an intercalation and exfoliation process leads to a highly porous EG with an extremely low density, occupying a volume about 200~300 cc for one gram of EG. The advantages of the EG are many. They are light, strong and stiff. Because EGs have a high degree of graphitic order, they are extremely thermally and electrically conductive along the graphite layer direction[1-7]. The nano-flake in the EG has a thickness of 20~50nm, about equal to the diameter of carbon nano-tubes. For this reason, EGs possess many features that CNTs have. Yet the most obvious advantage is that they are much less expensive compared with CNTs. This work examines the fabrication of composites using EG as reinforcement. The dispersion of the EG results in the nano-flake graphite, which was then added into the epoxy resin. These composites represent the same reinforcing material with different geometrical aspects. How this affects its mechanical behavior was studied.

2 Material Processing

The processing of the EG for this work has been previously reported [8]. To tear apart the nano-flake graphite (NFG) from the EG, many techniques have been employed, including rotational mixing, sonication and high shear-rate mixing. The nano-flake graphite composite is termed NFG/epoxy in this paper.

Three types of composites were made: the NG/epoxy, the EG/epoxy, and the NFG/epoxy. The weight contents of the additives were varied from 1~5%. To make NG/epoxy, the desired amounts of NG and the hardener were added to the epoxy. A mechanical mixer was used to disperse the NG into the epoxy. Since the NG is much heavier than the epoxy, the dispersed NG/epoxy was cured under a slow and constant rotation, preventing the NG from depositing to the bottom of the mold. The cured NG/epoxy composite was then released from the mold and cut into pieces of desired sizes for testing.

The EG/epoxy was made differently. To reduce air trapped within the EG, the EG was added into the epoxy under a vacuum condition. Since the EG is air-borne, care must be taken to prevent the

EG from sucking into the vacuum pump. Then the EG/epoxy was mechanically mixed lightly. Unlike NG, the EG is too light to drop within the viscous resin, and the rotation is unnecessary during curing of the EG/epoxy.

The NFG/epoxy was made form a mixture of EG/epoxy. The separation and dispersion of the NFG involve using a combination of rotational mixing, sonication, and high-shear mixing. The goal is to tear apart the NFG from the EG as thin as possible and disperse them in the epoxy as uniform as possible. The microscopic examination allowed us to assess how the goal was achieved.

2. Microstructures

The graphite in these samples varies in its geometric form. The thickness of NG is about 10~20 μm; the thickness of NFG is about 20~50nm, about 200~500 times thinner than NG. The crosswise size of NG is about 300~500 μm, while that of the NFG is less than 50 μm in general. The significant reduction in size is mainly because of the processing for separation and dispersion leading to fracture of the thin graphite sheets. Despite this, the aspect ration of the NFG is still as high as 1000.

The EG, composed of connected graphite sheets, has the crosswise size of the NG. The thermal shock expands the tightly stacked graphene layers along the transverse (*c*-axis) direction (Fig.2). The graphite sheets, which will later become NFG, are sharply bended to create large space inside the EG during the expansion. At this nano-scale, the graphite sheets behave in a flexible manner. Even under such an extremely high distortion, the graphite sheets remain intact. This exceptional flexibility, also seen in carbon nano-tubes, is non-existent in its macro-scale counterparts, such as NG and carbon fibers.

Fig.1 A piece of the natural graphite (NG) used in this work

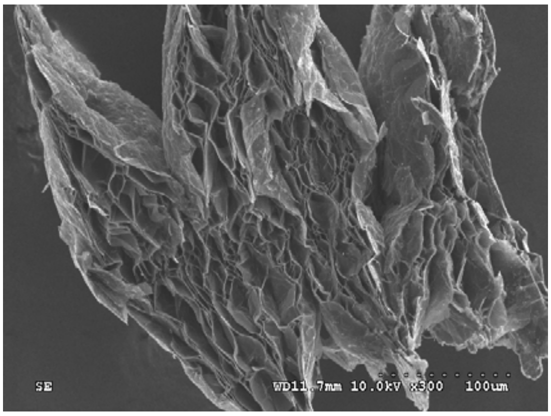


Fig.2 A piece of the expanded graphite (EG), showing exfoliated but still partially connected graphite sheets

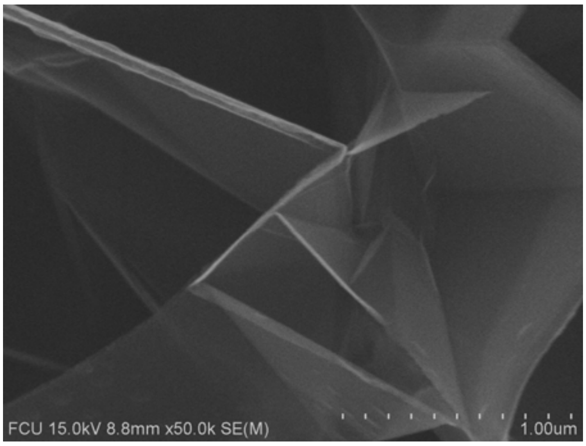


Fig. 3 Micrograph of the EG, showing sharp bending and exceptional flexibility of the graphite sheets

3. Thermal Conductivity

Both NG and EG were used to make specimens for thermal conductivity. The specimens were made by a direct compression of the material. Through the interaction of van der Waals force, the specimens were solidified under sufficient compression without any binder or resin. The compressive pressure was varied in a controlled manner to make samples of different densities. The compression resulted in layered structures with graphite layers roughly normal to the compressive direction.

Two types of samples were made, as shown in Fig.4. The first has a penny shape with 12.7mm in diameter. This is to measure the K values transverse to the graphite layers. The second type is a 8mm×8mm square shape. This is for measuring *K* values along the graphite layers. To make this, a bigger cylinder, same as the first type except the thickness is higher then 8mm, was made. Then the cylinder was carefully ground to shape with graphite layers parallel to the thickness direction. Figs.5 and 6 are cross-sections of the compressed EG, showing the stacking of the graphite layers. With a high pressure, the sample becomes more compact, and the void content is lower.

The measurements were conducted by using a Laser Flash. A laser beam hit the specimen on one side, and the rise of temperature on the other side was measured. From the temperature rise, the thermal diffusivity was calculated, and the thermal conductivity (K) can be calculated from the following equation:

$$K = \alpha \rho C_p \qquad (1)$$

where α is the thermal, ρ is the density, and C_p is the specific heat.

The results for the K values normal to the graphite layers are shown in Fig.6, and Fig.7 shows the results in the parallel direction. The densities vary from 2.05 to 2.2 for the NG, and from 0.38 to 1.05 for the EG. The NG must be very dense to be solidified. The K values range from 4 through 16 W/mk. In general, the K is proportional to the density of the material. With a higher density, the contact between graphite layers are closer, and the heat transfer is more effective, resulting in a higher K. For compressed NG, the K in parallel direction is more than 400 W/mk, which is about 25 times higher than that in the normal direction.

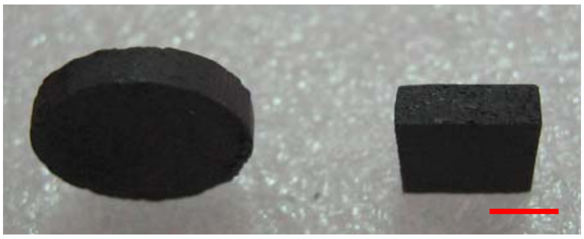
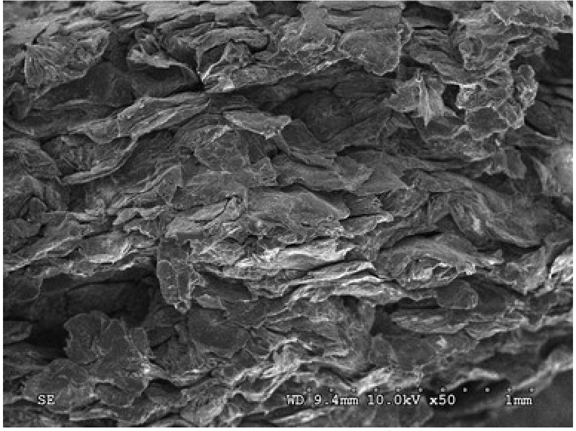
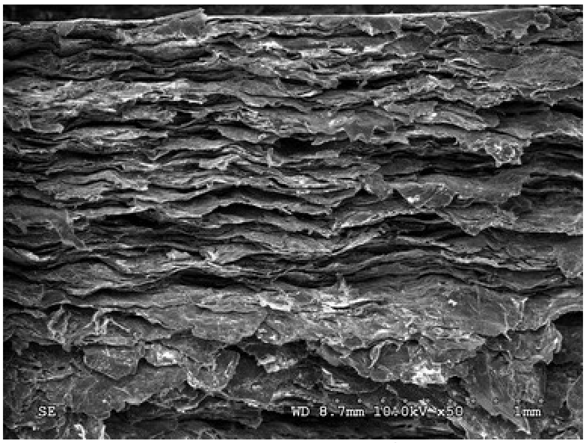


Fig.4. Samples for measuring thermal conductivity (bar: 4mm)



(a) $\rho = 0.46$ g/cm^3



(b) $\rho = 1.02$ g/cm^3

Fig.5. The compressed EG of different densities

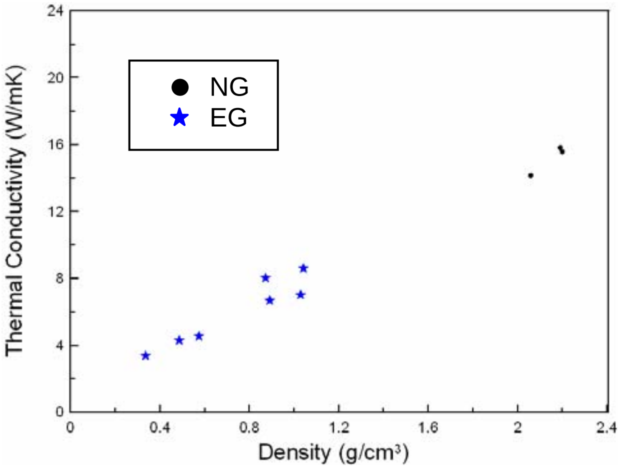


Fig.6. Measured thermal conductivity for samples with graphite layers normal to test direction.

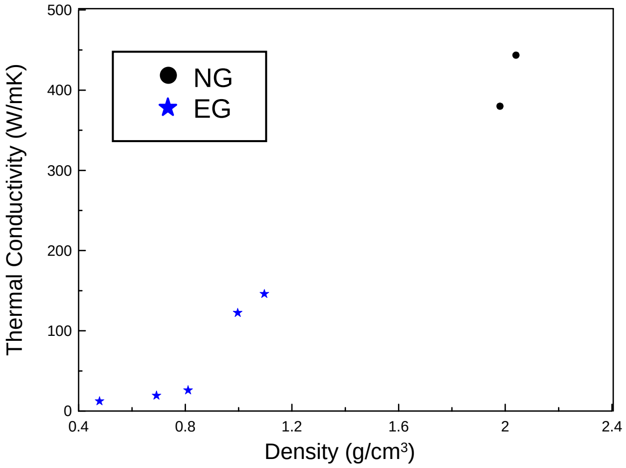


Fig.7. The measured thermal conductivity for samples with graphite layers parallel to test direction.

4. Compressive Test

The sample sizes for the compressive test were 10×10mm in cross-section and 50mm in height. The test was conducted by using an end-loaded fixture without any side support. The load was applied through a flat steel plate. The overhead speed was set at 0.5mm/min. The overhead was stopped when the induced load drops by 30% of the highest load. No structural buckling was observed. In some cases the load drops from the yielding point but then regains with strain to a level even higher than the yielding point. This often happens in short, thick, and ductile specimens. In that cases the load could never drop and the test was terminated manually. The compressive strength is defined as the local maximum stress.

Two materials were tested, the EG/epoxy and NFG/epoxy. A typical fractured surface of the NFG/epoxy is shown in Fig.8. The present materials are relatively ductile. When compressed, the materials become laterally expanded, rather than developing a inclined, fractured plane usually seen in brittle material. Thus, there is no sudden-drop in the loading curves, and the maximum stress is where the load becomes flat. The results for the compressive strength are shown in Fig.9. The microscopic observation revealed that the resin is unable infiltrate into the EG, in which the space inside the EG is too small for the viscous resin to flow into. Introducing EG into the resin also means bringing voids into the resin. Thus, the compressive strength is decreased with the weight fraction. For the NFG, the problem is much lessened. The drop in stress is not significant. Yet the NFG still has not provided reinforcing effect. One reason is that the overall NFG content is still too low to show such improvement. Another is the bonding between the NFG and the resin, which needs to be improved through functionalization on its surfaces.

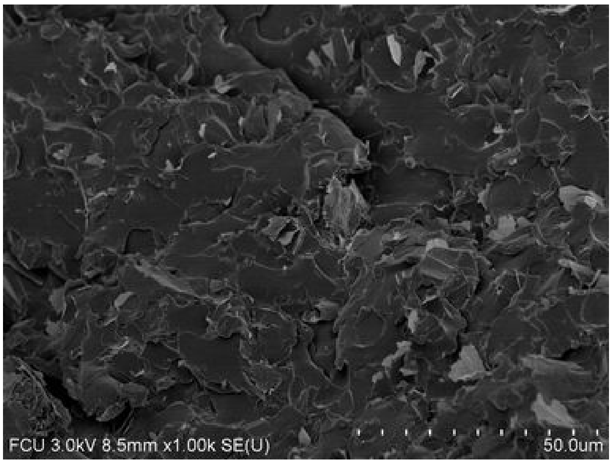


Fig.8. A typical fractured surface of the NFG/epoxy, showing separation and dispersion of the NFG

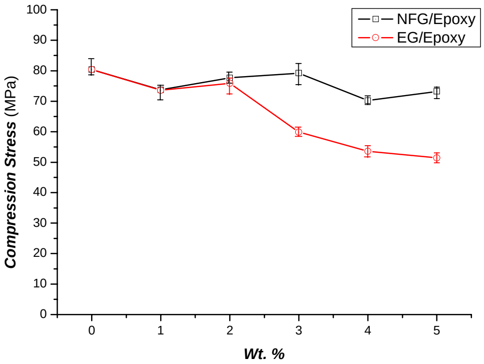


Fig.9. The measured compressive strengths for the EG and NFG samples

5. Impact Test

The Izod impact tests were conducted according to the ASTM D256-06a. The specimen was 10mm in width, 12.7mm in thickness and was notched by 2.54mm, leaving a 10.16mm in depth at the notch. The impact point was 22 mm above the notch. The impact energy was 3J, and the net energy absorbed by the specimen was measured. The surfaces of the fractured specimens were examined by SEM.

The results are shown in Fig.9. Both NG/epoxy and EG/epoxy show a decrease capability of energy absorption. One reason, as mentioned, is that adding the EG also introduces voids inside the EG. The nano-flakes inside the EG lack the access to epoxy and have little structural integrity. The NG/epoxy is slightly higher than the EG/epoxy, because NG is more compact and the resulting void content is much lower.

Figs.10 and 11 are the fractured surfaces of the NG and EG composites after the Izod impact tests. The fractured surfaces show ripple-like lines in the matrix (Fig.10), and the growth of these ripple lines were obviously affected by the existence of the NG. A piece of embedded EG can be seen in Fig.11. The The fractured surface is relatively flat and smooth.

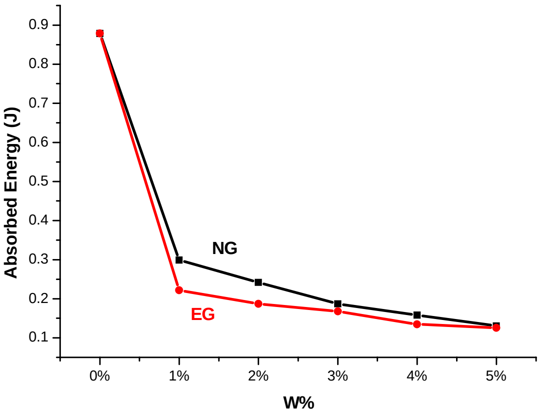


Fig. 10. The absorbed energy for the NG/epoxy and EG/epoxy

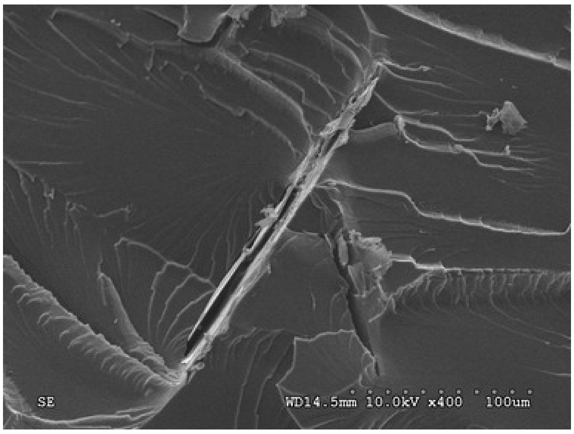


Fig.11. A fractured surface of the impacted NG/epoxy composite (5w%).

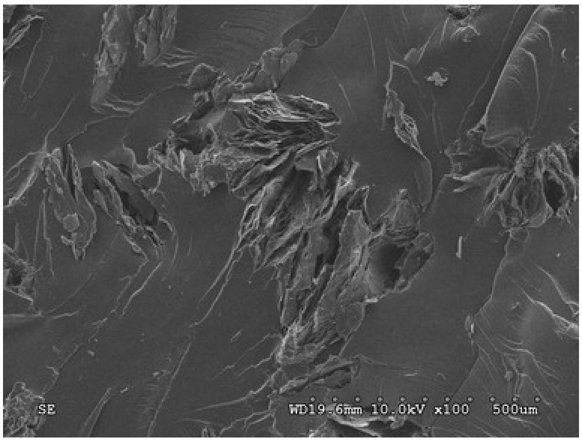


Fig.12. A fractured surface of the impacted EG/epoxy composite (5w%).

6. Conclusions

The paper made an attempt to examine the expanded graphite in the directly compacted form and in the composite form. Results revealed that the compacted NG can reach a density of 2.1g/cc, and a *K* value of 450 W/mk, while EG can reach a density of at least 1.1g/cc, and a *K* value of 150 W/mk. Along the transverse direction, the *K* value is 25 times lower than that in the parallel direction. In the composite form, the NG, EG, and NFG can all be dispersed uniformly in the resin. Their compressive and impact behavior have been examined. Results showed that the EG composites drop in the compressive strength and energy absorbing capability more notably, because voids within the EG are too small to be infiltrated by resin under normal pressures. With the dispersion technology, the nano-flake graphite sheets can be separated from the EG. The void problem has been eliminated in the NFG composites, and the compressive strength has been improved. To further take advantage of the nano-scale graphite, an appropriate surface treatment is needed in order to enhance wetting of the NFG.

Acknowledgement

The authors wish to thank the National Science Council of Taiwan, R.O.C. (NSC 94-2216-E-035 -013) for the support of this research.

References

[1] Kang Feiyu, Zheng Yong-Ping, Wang Hai-Ning, Nishi Yoko, and Inagaki Michio, "Effect of preparation conditions on the characteristics of exfoliated graphite", *Carbon*, Vol. 40, pp1575-1581, 2002.

[2] Chen Xiling, Song Kwmin, and Li Jihlt, "Preparation of lower-sulfur content and expandable graphite", *Carbon*, Vol. 34, pp 1599-1603, 1996.

[3] Song Kemin, and Huijuan, "On lower-nitrogen expandable graphite", *Materials Research Bulletin*, Vol. 35, p425-430, 2000.

[4] Inagaki Michio, Tashiro Ryuichi, Mashino, and Toyoda Masahiro, "Exfoliation process of graphite via intercalation compounds with sulfuric acid", *Journal of Physics and Chemistry of Solids*, Vol. 65, pp 133-137, 2004.

[5] Manning Thomas J., Mitchell Mike, Stach Joseph, and Vickers Thomas, "Synthesis of exfoliated graphite from fluorinated graphite using an atmospheric-pressure argon plasma", *Carbon*, Vol. 37, pp 1159-1164, 1999.

[6] Tryba Beata, Morawaski Antoni W. Kalenczuk Ryszard J. and Inagaki Michio, "Exfoliated graphite as a new sorbent for removal of engine oils", *Spill Science & Technology Bulletin*, Vol. 8, pp 569-571, 2003.

[7] Shen Wanci, Wen Shizhu, Cao Naizhen, Lu Zheng, Zhou Wei, Liu Yinghie, and Gu Jialin, "Expanded Graphite-A New Kind of Biomedical Material", *Letter to the Editor/Carbon*, Vol. 37, pp 351-358, 1999.

[8] Lu Hsin-Fang, Kuo Wen-Shyong, Ko Tse-Hao, "On The Microstructures and Thermal Conductivities ff Exfoliated Graphite," SAMPE 2006, Long Beach, April 30~May 4, 2006.