

A simple method to determine the surface energy of graphite

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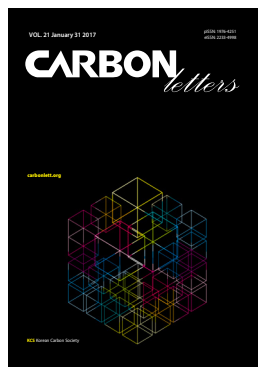
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Graphite is a material condensed from aromatic hydrocarbon that forms an infinite plane that exhibits an amphoteric feature. Structurally, a number of benzene rings form a solid planar sheet. A number of layers are formed from numerous unit cells, a so-called grapheme. A graphene sheet has an electron structure, which expands π -electrons into a two dimensional space. Graphite has AB-stacked bilayers of graphene. Because the interaction between two sheets is weak, their electronic structure may vary significantly. In addition, because graphite has either zero-semiconductor electronic structures, or a semi-metal electronic structure, its ionization energy is 4 eV [1] and it has dual electronic characteristics. Thus, it may work as either an oxidizer or reducer. In particular, the shape of the graphite plays an important role in its mechanical characterization [2]. Graphene, in its role as a unit cell of graphite, is known to have great potential for applications in many fields [3]. It is critical to understand graphite's interfacial interaction with a matrix, or its wettability, when applying its electrically and thermally conductive properties to characteristic composites.

In this study, we proposed a simple method by which to determine the surface energy of graphene to expand graphite applications and to understand better the interfacial interaction of various matrices. This will explain why strong acids (e.g., sulfuric acid and nitric acid [4-7]) are employed for graphene or graphene oxide synthesis. In order to implement these kinds of experiments, repetitive work and trial-and-error are unavoidable. However, if we are able to understand the surface energy of graphite, we can save time and effort as well as facilitate systematic approaches by which we can choose appropriate solvents and chemicals.

The surface energy could be represented in terms of wettability and contact angles. Wettability plays a key role in various industrial applications (e.g., material dispersion and interfacial chemistry). In particular, it significantly affects the coating industry, which includes nano engineering, ink, paint, paste, and adhesives; as well as the compound industry, which includes extrusion, injection molding, and casting [8-13]. Surface energy is the energy created by surface atoms, and is the result of the force of attraction they exert on external materials. Higher surface energy promotes greater liquid wettability. Therefore, the higher the surface energy is, the more enhanced the wettability, and the smaller the contact angle, becomes. As a result, knowing the droplet contact angle will determine the corresponding surface energy. The density of surface energy for water is 72 mJ/m² and its surface tension is 72 mN/m. Their values are the same. In order to measure the droplet contact angle, a planar surface and knowledge of the compact density of the given materials are required. In the case of graphite, it is difficult to acquire a planar surface. However, in this study, we report a simple method by which to prepare a planar surface of high-density graphite without using chemicals or binders. Without using complicated instruments, this method utilizes a pellet press for an infrared (IR) spectrometer, with which most general laboratories are equipped. Such a high-density surface, fabricated at room temperature, was used to measure surface angles of water droplets (as a polar solvent) and diiodomethane (DIM) droplets (as a non-polar solvent). By using the acquired angles, we were able to calculate the surface energy.

The natural graphite (NG) used in this experiments had a bulk density of 0.28 g/mL, and size less than 200 mesh (<75 μ m). Artificial graphite (AG) has a bulk density of 1.02 g/mL, and a size less than 100 mesh (<150 μ m). The bulk density was measured by reading the final volume of a sample after tapping it 1000 times in a tap density meter, which initially filled a 10 mL mass cylinder, and was weighed. In order to precisely measure the contact angle,

the measuring surface has to be planar and compact. However, because of graphite's high lubricity, it is extremely difficult to construct a densely packed structure of graphite, without pores. Therefore, some researchers tried to use a filtration apparatus to form a free standing film [3], or use a binder to form a particular shape. In order to prepare a planar surface of high-density graphite, we used an Evacuatable Pellet Press (PIKE Technologies, USA) to pressurize a 0.2 g sample and maintain its pressure for a while. A hydraulic press served as a pressurizer for the NG. NG, which has many grades, can be relatively hygroscopic because it has intrinsic chemical structure (e.g., oxygen-containing functional groups). Besides functional groups, moisture can affect the density of NG when it is compressed; therefore, NG needs thermal treatment. Although the high-temperature treatment has the advantage of purity, it is costly. Furthermore, there is concern for the deformation of graphite structure. Before the compression experiments, the physically adsorbed moisture was dried out of the graphite by exposure in a preheated oven for a day at 60°C. In the case of AG, a hydraulic press could not be used to do the packing; so a molding press that enabled higher pressure was employed. The purity of the prepared graphite was confirmed using a thermogravimetric analyzer (TGA-DSC1 model; Mettler-Toledo Inc., USA) Measurement conditions include a heating rate of 5°C/min and a range of temperature from 25 to 950°C. A solvent for measuring contact angles, DIM (99% purity), was acquired from Sigma-Aldrich, USA. The instrument used to measure the contact angle was a Phoenix 300 model (Surface Electro Optics, Korea). A syringe of 10 mL volume was used when measuring the contact angle. The distance between the apex of the needle and the sample surface was maintained at 15 mm. After a solvent droplet was formed on the surface, a magnifying camera was used to measure the contact angle.

In Fig. 1a and b are the results of contact angles of water and DIM, respectively, on the surface of NG. Fig. 1c and d represent contact angles of water and DIM on the surface of AG. Graph-

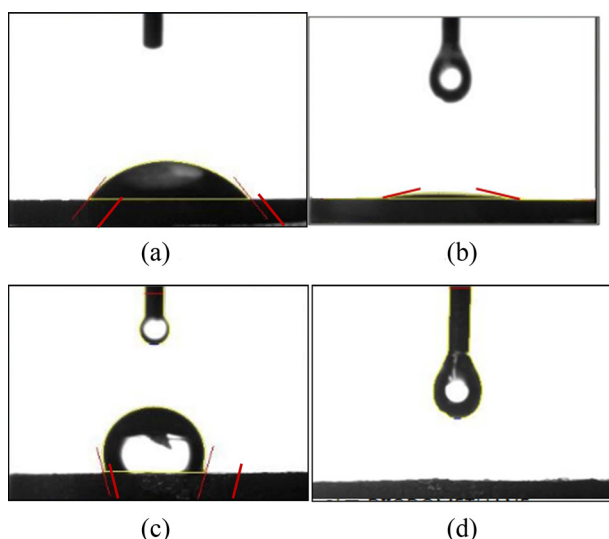


Fig. 1. Photographic images of contact angles per solvent on a high-density graphite surface, (a) NG@water and (b) DIM, (c) AG@water and (d) DIM. NG, natural graphite; DIM, diiodomethane; AG, artificial graphite.

ite consists almost entirely of carbon and hydrogen atoms, and also has high surface energy and hydrophobic characteristics. If graphite meets water (highly polar), they repel each other, while graphite has high affinity for DIM. Because water has a hydrophilic characteristic and DIM has a hydrophobic characteristic. Fig. 1c shows the contact angle of AG is larger than NG's Fig. 1a. However, Fig. 1d shows that the contact angle of AG is smaller than that of NG Fig. 1c.

The difference between the contact angles measured for NG and AG depends on their crystal structures, level of defects, and purity [14-19]. The purity of the graphite was confirmed using thermo-gravimetric analysis in a common air environment (Fig. 2). The residue after combustion at 950°C was mostly composed of inorganic elements or carbon flakes that were not combusted in a high temperature environment. The residue of NG was approximately 2 wt%, while that of AG was approximately 0.35 wt%. As a result, the residue of NG contained more heterogeneous materials than that of AG because artificial graphite goes through a harsh calcination process at a high temperature of >3000°C [20]. Therefore, NG has more cohesive force because of greater molecular interaction. On the other hand, AG has a relatively higher purity so that the packing of AG is challenging and requires a higher pressure to achieve a high-density surface (Fig. 3a). A high-density NG graphite sample was maintained at a relatively low pressure of 10 ton/cm² for 4 h while AG was maintained at 20 ton/cm² for 12 h (Fig. 3b)

The contact angles measured on fabricated surfaces with different solvents differed significantly. Many theories have been developed related to the calculation of surface energy. Among them, we chose the Owens-Wendt geometric mean equation [21,22].

$$\gamma_L = (1 + \cos \theta) 2(\gamma_S^D \gamma_L^D)^{1/2} + 2(\gamma_S^P \gamma_L^P)^{1/2} \quad (1)$$

Here, represents the dispersion term of surface energy, stands for the polar term of surface energy, θ represents contact angle, S stands for "solid", and L stands for "liquid". Using the contact angles of the solvents selected (water and DIM), we were able to derive the graphite's surface energy.

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (2)$$

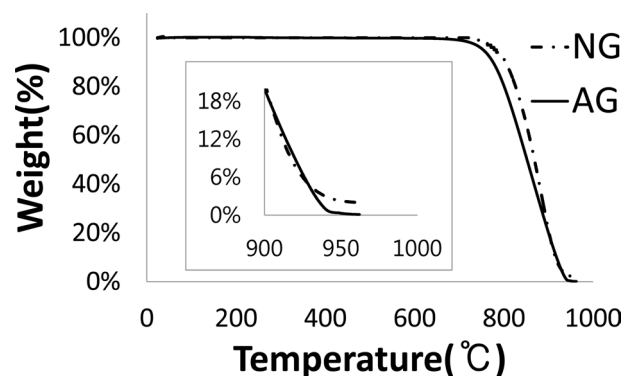


Fig. 2. Thermogravimetric analysis of NG and AG acquired using a thermogravimetric analyzer. The dotted line indicates NG, and the solid line indicates AG. NG, natural graphite; AG, artificial graphite.

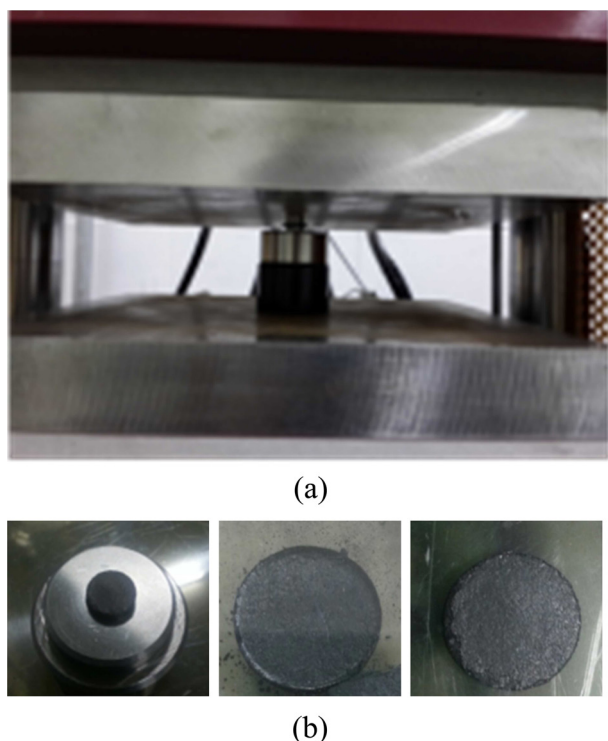


Fig. 3. Processing of an AG pellet for measuring a liquid droplet contact angle: (a) a molding press equipped with an Evacuatable Hydraulic Press is used. (b) A high-density graphite pellet. Photographs of graphite pellets after being pressurized in a molding press: NG pellet (left) and AG pellet (right). NG, natural graphite; AG, artificial graphite.

Table 1. Contact angles with water and DIM at 25°C

Graphite	Water	DIM
NG	53.8 ± 2.7	3.9 ± 0.6
AG	103.7 ± 1.3	0.0 ± 0.0

DIM, diiodomethane; NG, natural graphite; AG, artificial graphite.

Table 2. Owens-Wendt geometric parameters for water and DIM at 25°C

Graphite	(mN/m)	(mN/m)	(mN/m)
NG	50.71 ± 0.06	11.71 ± 1.42	62.43 ± 1.37
AG	50.8 ± 0.00	0.60 ± 0.18	51.41 ± 0.18

DIM, diiodomethane; γ , dispersion component; γ_p , polar component; γ_t , total surface tension; NG, natural graphite; AG, artificial graphite.

The contact angle (θ) measurements from high-density pellets of NG and AG are demonstrated in Table 1.

In this case, dispersion components (γ_d) of water and DIM were (26.4 and 50.8) mN/m, respectively. The polar components (γ_p), were (46.4 and 0.0) mN/m, respectively (Table 2). The surface energy of graphite can be acquired from a quadratic equation derived from the contact angle between water and DIM, and the graphite surfaces. For example, when the contact angle between

NG and water was 51.1°, this contact angle could be entered into eq 1, along with the dispersion component and the polar component, as displayed in Table 2.

Then, eq 1 becomes an equation (eq 2) that relates γ_t and γ_p . Using the same method, and the DIM contact angle (4.5°), we were able to create another equation relating γ_t and γ_p . By solving this quadratic equation, $\gamma_d = 50.64$ mN/m and $\gamma_p = 13.29$ mN/m can be acquired. The summation of the two values yields the surface energy of NG (63.93 mN/m). In the same way, we were able to acquire the surface energy of AG (51.41 mN/m). The calculated surface energy was obtained by averaging quintuplicate measurements of contact angles. Understanding the characteristics of the surface energies and obtaining those values will enable us to predict the compatibility of graphite with a matrix, or predict their interfacial interactions. In addition, because it may also decrease the number of required experiments by predicting the most optimal wetting solvent, it could become a simple, yet powerful, method for selecting matrices or solvents.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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