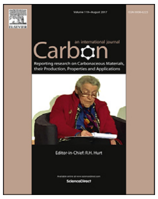
Carbon 119 (2017) 40–46

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon



Volume control of expanded graphite based on inductively coupled plasma and enhanced thermal conductivity of epoxy composite by formation of the filler network

Hyun Su Kim [a, b, 1], Jong Hyeok Kim [a, b, 1], Woo Young Kim [a], Hun Su Lee [a], Seong Yun Kim [a, *], Myung-Seob Khil [b, **]

[a] *Multifunctional Structural Composite Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk, 55324, Republic of Korea*

[b] *Department of Organic Materials and Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonbuk, 54896, Republic of Korea*

ARTICLE INFO

Article history:
Received 15 March 2017
Accepted 8 April 2017
Available online 10 April 2017

ABSTRACT

Expanded graphite (EG) is noticed as a thermally conductive carbon filler because of its advantages of a unique structure in which graphite sheets are intercalated and relatively a low price among carbon fillers. Nevertheless, the relationship between the volume expansion (≈interlayer spacing) of EG and the thermal conductivity of EG filled composites has been rarely reported on. We designed and developed an inductively coupled plasma (ICP) for the rapid expansion of a expandable graphite precursor. Greater extent of volume expansion of EG was observed at higher ICP treatment temperature and the thermal conductivity of the composites was increased with the expanded volume of the filler, at the same filler content. Based on a quantitative analysis on filler size within the composites using non-destructive micro-computed tomography, larger size of three dimensional (3D) thermally conductive filler networks with respect to the volume expansion were obviously confirmed. Excellent thermal conductivity (the highest value of 10.77 W/m·K) and heat dissipation characteristic of the composites were derived when the 3D thermally conductive EG filler network was generated at a larger size. These findings can contribute to realizing effective and low-priced thermally conductive carbon filler based polymer composites.

1. Introduction

Integration of electronic devices can cause problems such as heat shock and fire by preventing the heat generated inside the device from being released [1–3]. Hence, there is a growing interest in thermal control of integrated electronic devices. In particular, the fabrication of electronic device housings and heat dissipation structures for light emitting diodes requires the development of thermally conductive polymer composites that are advantageous in terms of the process and product degree of freedom [3,4]. Because thermally conductive polymer composites are fabricated by incorporating conductive fillers such as ceramics or metals into polymer resins [1–13], great attention is being paid to such nanocarbon fillers as graphene [6–8] and carbon nanotubes [8–10] which have been reported so far to have very high thermal conductivity, in a range of 1950–6500 W/m·K [14–19].

In polymer composites filled with perfectly dispersed carbon fillers, interfacial thermal resistance is the most significant physical factor that determine the thermal conductivity of the polymer composites [5–13,16,20]. In terms of quantum physics, the interfacial thermal resistance indicates the phonon scattering at interfaces between the carbon fillers and the polymer matrix. From a materials science aspect, this means a structural mismatch in terms of the vibration energy transport between the crystalline carbon and the polymer chain structures [16,20–22]. In polymer nanocomposites containing nanocarbon fillers, the interface thermal resistance can be maximized by increasing the interface amounts and by establishing incomplete contact between the nanocarbon fillers and the polymer matrix [11,16,20]. For example, Huxtable et al. [21] reported that “heat transport in a nanotube composite

---

* Corresponding author.
** Corresponding author.
E-mail addresses: sykim82@kist.re.kr (S.Y. Kim), mskhil@jbnu.ac.kr (M.-S. Khil).
[1] The authors contributed equally to this work.

http://dx.doi.org/10.1016/j.carbon.2017.04.013
0008-6223/

material will be limited by the exceptionally small interface thermal conductance (G ≈ 12 MW/m^2 K^1)". As a result, polymer nanocomposites show thermal conductivity values close to the lower bound of the rule of mixtures [16].

Unlike the electrical percolation phenomenon for polymer composites filled with carbon fillers, contradictory findings for thermal percolation phenomenon have been reported [1,23–28]. Some studies [25,26] have demonstrated continuous linear enhancement of thermal conductivity; others [1,27,28] have shown thermal percolation behavior. Shtein et al. [1] insisted that they found strong evidence for thermal percolation phenomenon in a polymer composite highly filled with graphene nanoplatelet (GNP) and that the thermal percolation was caused by direct contact between the incorporated fillers. Although phonon scattering can be generated by thermal contact resistance caused by incomplete contact between carbon fillers, phonon scattering due to interfacial thermal resistance is generally larger than that due to the thermal contact resistance [16]. Therefore, to maximize the thermal conductivity with thermal percolation, the introduction of fillers in direct contact within polymer matrix is preferable by switching the phonon scattering mechanism from the interfacial thermal resistance to the thermal contact resistance [16].

Expanded graphite (EG) is a uniquely-structured form of carbon filler in which graphite sheets are intercalated. When mixed with polymers, the EG can be effectively filled in composites because it forms an ideal thermally conductive network similar to that of the directly contacted graphite structure. Noh and Kim [11] evaluated the thermal conductivity of composite materials fabricated with various carbon fillers including EG, pitch-based carbon fiber, graphite, GNP, multi-walled carbon nanotube and carbon black, and reported that EG-containing composites exhibited the highest thermal conductivity. Furthermore, among carbon fillers, EG is relatively cheap and thus advantageous in terms of commercialization. For these reasons, EG is attracting attention again as a thermally conductive carbon filler. Nevertheless, there have been few organized studies on the relationship between the volume expansion (≈interlayer spacing) of EG and the thermal conductivity of composites.

Expandable graphite (EaG) as a precursor of EG is usually manufactured by acid treatment of graphite. When EaG is heat-treated at high temperatures, graphite layers are expanded by the evaporation of small oxides on the layer surfaces. In an attempt to shorten furnace-based heat treatment processes that require long processing times for temperature elevation and cooling, this study treated EaG at different temperatures using an inductively coupled plasma (ICP) and adjusted the volume expansion. Further, composites were prepared using a fabrication method that was able to maintain the morphology of EG by inducing a high level of dispersion by means of ultrasound because composite fabrication techniques based on high-shear mixing may cause a change in the volume expansion of EG or in the morphology of the graphite layers, due to the use of high-shear forces. After measurement of the thermal conductivity of the composites, the relationship between the volume expansion and the thermal conductivity was discussed based on a quantitative size analysis of three dimensional (3D) thermally conductive filler networks using non-destructive micro-computed tomography (micro-CT) technique.

2. Experimental

2.1. Materials

EaG powder (ES 250 B5D) was obtained from Samjung CNG (Gyeongbuk, Korea). This material has a layered graphite morphology, as can be seen in Fig. 1a, and shows a carbon content of 95% and an expansion rate of ≥250 cm^3/g per min. The graphite powder began to expand at above 200 °C; its grain size was 296 μm. An epoxy resin and hardener (YD128, Kukdo Chemical, Seoul, Korea) were used as polymer matrix.

2.2. ICP treatment

Typically, furnace-based heat treatment requires a long processing time, as materials are slowly heated or cooled to a target temperature to avoid possible damage due to heat shock. In this work, we directly designed and fabricated ICP equipment as shown in Fig. 2; the ICP was used to shorten the treatment time for expansion of the EaG fillers. In order to expand EaG fillers, power input to the antenna in the ICP system was controlled to set the gas temperature at 400, 600 or 800 °C under Ar of 200 mTorr for only 20 min as shown in supplementary video.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.04.013.

2.3. Defect level

Raman spectroscopy (LabRAM HR 800, HORIBA Jobin Yvon, Japan) was employed to evaluate structural defects in the EG fillers with respect to the treatment temperature of the ICP process; Raman analysis was performed using a 514 nm Ar ion laser.

2.4. Functionality

Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific, MA, USA) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, Massachusetts, USA) were used to analyze the functional groups of the ICP treated EG fillers. FT-IR spectra were measured in the range of 500–4000 cm^{-1} at a resolution of 16 cm^{-1}. XPS spectra were obtained with an Al X-ray source under a pressure of 1×10^{-8} Pa.

2.5. Composite fabrication

Applying a high-shear mixing technique for the fabrication of composites can cause a change in the volume expansion or in the morphology of EG. In this work, therefore, composites were prepared using a manufacturing process that was able to maintain the morphology of EG. After mixing of the epoxy resin and hardener in a volume ratio of 1:1, the EaG or ICP treated EG fillers were mixed with the prepared matrix under ultrasonic conditions for 30 min. The fully dispersed epoxy mixture was hardened for 20 min at 80 °C.

2.6. Morphology

The ICP treated EG samples were obtained in powder form, and the fabricated composites were fractured in liquid nitrogen for sampling. The prepared specimens were surface-coated with platinum for 120 s in a vacuum using a sputter coating machine (Ion Sputter E-1030, Hitachi High Technologies, Tokyo, Japan). The coated EG and composite specimens were observed using a field-emission scanning microscope (FE-SEM, Nova NanoSEM 450, FEI Corp., OR, USA) with a voltage of 10 kV applied under nitrogen vacuum.

2.7. Thermal conductivity

The thermal conductivity of the composites was measured in accordance with the ISO 22007-2 standard using a conductivity-measuring instrument (TPS 2500 S, Hot Disk ab, Gothenburg,