Fabrication of Controlled Linear Assemblies of Graphite Flakes in Polysiloxane-based Nanocomposite Films and Enhancement of Thermal Property

Hong-Baek Cho[a,*], Shota Yanahara[a], Tadachika Nakayama[*], Hisayuki Suematsu[a], Tsuneo Suzuki[a], Weihua Jiang[a], Satoshi Tanaka[a], Yoshinori Tokoi[b], and Koichi Niihara[a]

[a]Extreme Energy-Density Research Institute, Nagaoka University of Technology,1603-1 Kamitomioka, Nagaoka , Niigata 940-2188, Japan, hong-baekcho@etigo.nagaokaut.ac.jp; nky15@vos.nagaokaut.ac.jp
[b]Department of Electrical and Electrics system Engineering, Nagaoka National College of Technology, 888 Nishikatakai, Nagaoka, Niigata 940-8532, Japan

ABSTRACT

Fabrication of polysiloxane-based nanocompoistes with linear assemblies of graphite flakes (GFs) are performed under application of electric and magnetic fields. Here, we firstly introduce that the longitudinal direction of GFs can orient and futher make linearly aligned structures anchoring the composite film surfaces with increSased thickness of the linear structure. The controlled variation of applied electric fields produde the denser linear assemblies of the GFs, which is directly related with the enhancement of thermal conductivity of the composites. The different effects of applied magnetic field and electric fields on the assemblies of GFs are eluciated.

Keywords: Graphite flakes, self-assembly, nanocomposites, electric field inducement, thermal diffusivity

1 INTRODUCTION

Polymer-based nanocomposites have showed rapid growth of interest either by scientific and electronic industries [1-3]. Because of the heat removal problem in the electric devices, the researches for development of thermal interfacing materials (TIMs) by incorporation of high thermal conducting nano-dimensional fillers are crucial issue. High thermal conducting fillers, such as, carbon nanotubes (CNTs) [4], graphite nanosheets (GNs) [5, 6], and boron nitride (BN) nanosheets [7], have been incorporated in fabrication of polymer-based nanocomposite with anisotropic orientation, because when the longitudinal direction of such 1-D and 2-D fillers are oriented perpendiculat to the composite film surface, the heat emittion through the high thermal conductive fillers across the composite film would be enhanced by avoiding the route though the polymer matrix [8]. TIMs are polymer-based composites with thermally conductive particles, which require high volume fractions of filler (up to 70%) to achieve K of ~ 1-5 W/mK[9] for the practical use. Many research groups have reported successful fabrication of to satisfy the given thermal property, but they are limited for practical application due to material's redundancy, economical and workability problems. Thermal conductivity of carbonaceous materials, such as, CNTs, nanodiamonds and graphites, are therefore have been widely used as fillers to fabricate high thermal conductive materials using small amount of fillers. Field-induced fabrication through orientation and relocation of GNs have been widely applied, but their accomplishment is limited to control only the direction of orientation in polymer matrix, which doesn't accompany the end-to-end attachment of fillers.

In the present research, we report successful control of orientation and relocation of GNs in polymer matrix using electric and magnetic fields inducing external torques. According to modulation of the external torque, GNs can establish end-to-end attachment anchoring film surfaces by self-assembly, and the intensity of the linear assembles of GNs (LAGFs) are modulated. The relationship between the LAGFs structure and enhancement of thermal property of the composites are investigated. AC, DC, switching DC electric fields, and magnetic fields are applied for the controlled orientation of GNs in polymer matrix.

2 EXPERIMENTALS

2.1 Materials and Fabrication of Ordered Polysiloxane/GFs Nanocomposites

Polysiloxane/GFs nanocomposite films were prepared by introducing GFs into a polysiloxane prepolymer mixture. Figure 1 shows SEM micrograph of GFs(Wako Pure Chemical Industries, Ltd.) with average diameters of 15 μm by magnification of a) × 5,000 and b) ×10,000. The images show that the graphite flakes have planar structure with several graphite nanosheets of nano-dimensional thickness. The amount of GFs added was 0.1%, 0.2%, or 0.3 vol.%. Two polysiloxane prepolymers with different viscosities were used: YE5822(A), viscosity: 1.2 Pa.s, Mw_{av}: 21,000, and YE5822(B), viscosity: 0.2 Pa.s, Mw_{av}: 16,000, (Momentive Performance Materials). An indium-tin oxide (ITO) coated glass slide (2.5×7.5×1.0 mm^3, Sigma-Aldrich), with 8-12 Ω/sq surface resistivity was used as an electrode for the application of the electric field. First, three grams of silicone YE5820(A) was sonicated for 5 min, and a mixture

of 0.3 g of silicone YE5822(B) and 0.416 g of GFs was introduced into the sonicated silicone YE5820(A) and further sonicated for 10 min. The mixture was stirred using a high-speed mixer at 1,500 rpm for 5 min to produce a homogeneous dispersion, which was then cast onto a glass spacer (1.2×1.2 mm^2×120 μm), which was located between the two electrodes (Fig. 2), and subjected to 0.2 kV AC (50 Hz), DC, or switching DC electric fields for 16 h to enhance the orientation and relocation of GFs in the polysiloxane prepolymer mixtures.

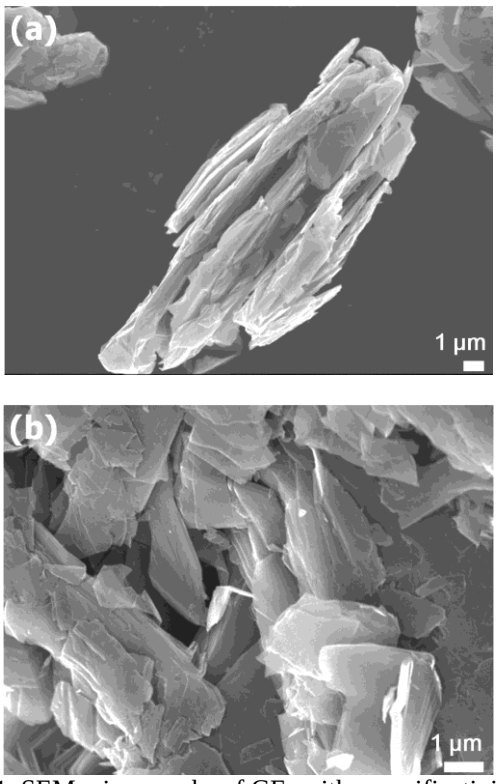


Figure 1. SEM micrographs of GFs with magnificatioin of a) × 5000, and b) × 10,000

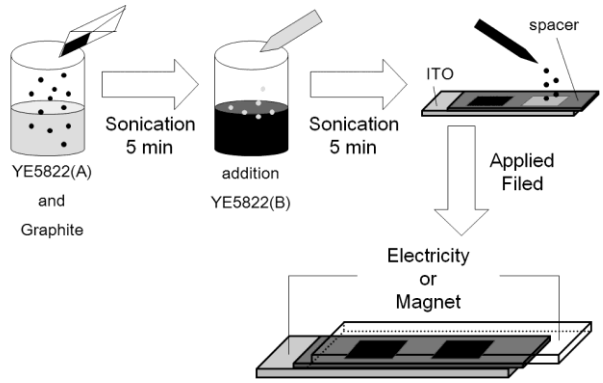


Figure 2. Illustration of experimental setup for incorporatioin of GFs under electric or magnetic field.

The polarity of the DC electric field was changed at 4 h intervals during the experiment. For the anisotropic orientation of GFs under magnetic field, the casted suspention between glass plate was applied under magnetic field of 0.5 T for 24 h. Finally, the prepared composites were dried for 0.5 h at 80℃ to ensure the complete curing of the composites.

2.2 Characterization

The anisotropic alignment of the GFs in the polymer films was analyzed by X-ray diffraction (XRD; Rigaku RINT 2500). The degree of orientation of the GFs perpendicular to the film surface was estimated by comparing the peak intensity scanned from 10° to 40° at a rate of 2°/min. Cukα, λ=0.15405 nm, radiation was generated under 40 KV and 40 mA of X-ray source.

The linear distribution of GFs in the polysiloxane matrix was observed by a digital microscope (Keyence VHX-9000) followed by cross-sectioning of the polymer/GFs composite films. The surface morphologies of GFs were observed using scanning electron microscopy (SEM; Jeol JSM-6700F).

2.3 Measurements of Thermal Property

The thermal diffusivities in the out-of-plane direction of the composite films were analyzed using a measurement system for thermal diffusivity by temperature wave analysis (ai-Phase Mobile 1), which was operated under frequencies ranging from 2 Hz to 81 Hz under room temperature, with an input voltage of 0.3 V and a data acquisition time of 0.2 s.

3 RESULT AND DISCUSSIOINS

3.1 The Orientation an Linear Assemblies of GFs in Polymer Matrix

Figures 3. shows that the X-ray diffraction patterns of GFs in the polysiloxane/GFs composite films. The sharp increase in the diffraction patern at 2θ=26.4◦ results from the (002) planes of GFs. The intensity of this peak decreases as the in-plane direction of the GFs is oriented perpendicular to the composite film planes. It is understood that the GFs with random distribution well aligned to perpendicular direction after application of electric and magnetic fields. The least peak intensity of GFs under application of magnetic field implies that the magnetic field is the most influential for anisotropic orientation of GFs in polymer matrix rather than other applied electric fields.

The cross-sectional observation, shows the assemblies of GFs incorporated in the polymer matrix as illustrated in Figure 4. The composites, prepared under application of electric fields, shows LAGFs anchoring the film surfaces, which is very different from the view of the composite, prepared under magnetic field application. The magnetic field induced the orientatioin of GFs with the high anisotropy, but couldn't enance the end-to-end attachment

of the fillers in polymer matrix. In addition, the application of switching DC resulted in the increased thickness of LAGFs composed of denser amount of GFs. This phenomenon could be confirmed by plane observations, (which is not posted here): the highest population of LAGFs was fabricated under application of AC, but the average thickness of LAGFs is the smallest. The electrid field switching under DC resulted in the lowest population of LAGF, while the motivated the formation of LAGFs with denser population of GFs rather than any other conditions of electric fields.

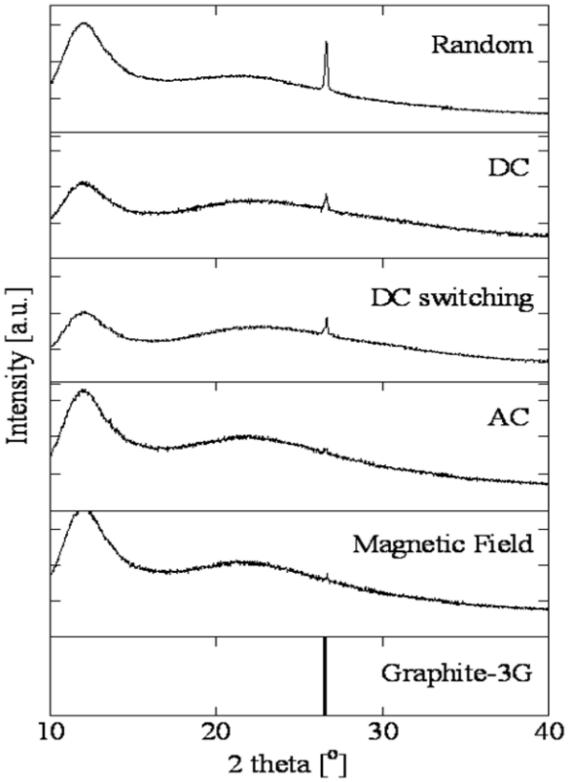
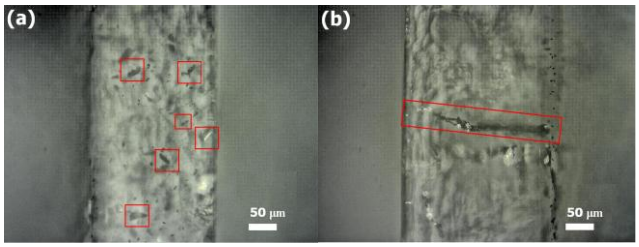


Figure 3. X-ray diffraction of polysiloxane/GFs nanocomposite films as a function of inducement conditions.



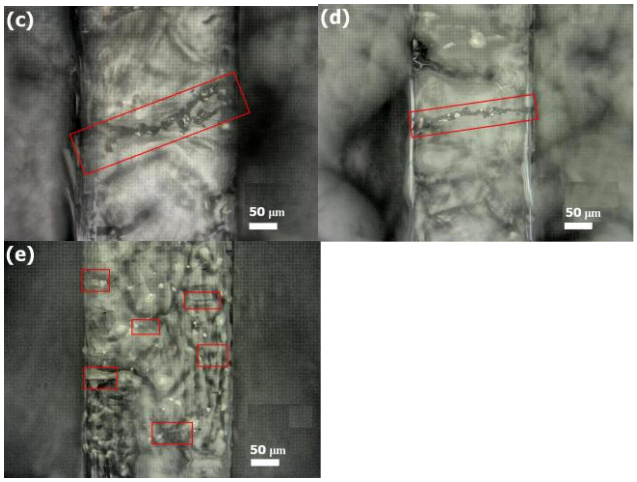


Figure 4. Digital micrographs of cross-sectioinal observation of composites: a) Random, b) DC electirc field, c) Switching DC electric field, d) AC electric field, e) Magnetic field.

3.2 Thermal Properties

Figure 5 shows thermal diffusivities of composites fabricated under different field conditions. Magnetic fiend enhanced the highest anisotropy of GFs, but couldn't motivate the end-to-end attachment of the fillers as described in Fig. 3~4. Figure 5 (a) shows that the composites prepared under DC electric field enhanced the thermal diffusivity higher than those prepared under magnetic field. The influence of different orientation sourfe got highered according to the increase of the filler content. When the influence of different electric fields was compared (Fig. 5(b)), the composites fabricated under application of switching DC showed the highest thermal diffusivities. Under application of electric field, the longitudinal ends of 1-D or 2-D electric or dielectric fillers are polarized and aligned to the direction of the electirc field [10]. The orientation and end-to-end attachment of electric or dielectric fillers are influenced by cordinated sources of Coulmb attraction, electrophoresis, and dipolarization under electric field-inducement [11]. This researches demonstrated the controlled application of electric fields can form linear assemblies of GFs and further increase the thickness of LAGFs in polymer while the polymer suspension was not completely cured.

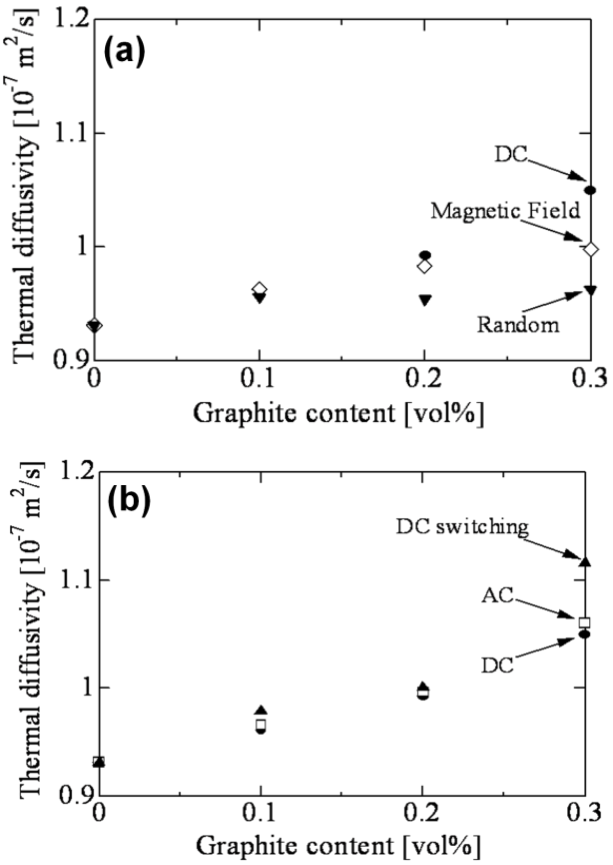


Figure 5. Thermal diffusivity of polysiloxane/GF nanocomposite films as a function of GF content; (a) under magnetic field and (b) under different electric fields.

4 CONCLUSIONS

Fabrication of linear assemblies of GFs(LAGFs) were accomplished in polymer-based nanocomposites, and the thickness of LAGFs were controlled under modulation of electric fields. Application of magnetic field motivated the highest anisotropic orientation of GFs among the applied external torque sources, but couldn't motivate the end-to-end attachment of the fillers. The formation and thickness variation of LAGFs were firstly demonstrated by controlled application of electric fields. Application of switching DC resulted in the smallest population of LAGFs in polymer matrix, while motivated the denser population of GFs, which attributed to the notecible enhancement of thermal conductivity of the composites. The authors believe that this modulation technique will pave the way for researches over fabricating nannocomposites with linearly aligned 1-D or 2-D nanofiller structures for their potential application in the semiconductor industry, such as, TIM.

REFERENCES

[1] I. Chasiotis, Q. Chen, G. M. Odegard and T. S. Gates, Exp. Mech. 45, 507, 2005.

[2] T. Takahashi, K. Suzuki, H. Awano and K. Yonetake, Chem. Phys. Lett. 436, 378, 2007.

[3] H. Wang, H. Zhang, W. Zhao, W. Zhang and G. Chen, Compos. Sci. Technol. 63, 225, 2003.

[4] F. Deng, Q.-S. Zheng and L.-F. Wang, Appl. Phys. Lett. 90, 021914/1, 2007.

[5] J. Lu, W. Weng, X. Chen, D. Wu and G. Chen, Adv. Funct. Mater. 12, 1358, 2005.

[6] H. Wang, H. Zhang and G. Chen, Compos. Part A-Appl. S. 38, 2116, 2007.

[7] H.-B. Cho, T. Nakayama, T. Suzuki, S. Tanaka, W. Jiang, H. suematsu and K. Niihara, J. Nanomater. 2011, 693454/1, 2011.

[8] H.-B. Cho, Y. Tokoi, S. Tanaka, T. Suzuki, W. Jiang, H. suematsu, K. Niihara and T. Nakayama, J. Mater. Sci. 46, 2318, 2011.

[9] A. A. Balandin, Nature Mater. 10, 569, 2011.

[10] H. Wang, H. Zhang, W. Zhao, W. Zhang and G. Chen, Compos. Sci. Technol. 68, 238, 2008.

[11] G. H. Kim and Y. M. Shkel, J. Mater. Res. *19*, 1164, 2004.