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Magnetic field-induced enhancement of thermal conductivities in polymer composites by linear clustering of spherical particles

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ABSTRACT

We developed linearly linked spherical fillers in polymer composites with incorporating Al_2O_3-Fe_3O_4 hybrid particles under a magnetic field to form thermal networks for high thermal conductivity. The Al_2O_3-Fe_3O_4 hybrid particles were prepared by a simple precipitation method and their magnetic properties were characterized with magnetic hysteresis. The Al_2O_3-Fe_3O_4 hybrid particles were well aligned through direction of magnetic field as confirmed by microscopic observation. The polymer composites obtained with Al_2O_3-Fe_3O_4 hybrid particles possessed high thermal conductivity in a parallel magnetic alignment direction at low filler loading, which is more than 240% outperformed the composites with randomly dispersed fillers.

1. Introduction

Development of modern electronic devices has led to a rapid increase in power density resulted from miniaturization and integration of device elements operated at high frequencies [1–10]. Then, efficient removal of dissipated heat is essential to maintain device performances and to ensure long lifetime span [9,10]. Among the various packaging materials for efficient heat dissipation of electronic devices, thermal interface materials (TIMs) are widely employed to relieve the thermal bottlenecks at the interfaces between heat sources (chips) and heat sinks [10–12]. Since TIMs are designed to fill the air gaps at the contact interfaces, polymer composites with moderate thermal conductivity and sufficient flexibility are popularly used. In the polymer composites, the poor thermal conducting ability of polymers was compensated by filling with inorganic fillers having high thermal conductivity and excellent electrical resistivity [5–7]. Among the numerous inorganic materials such as alumina (Al_2O_3), boron nitride (BN), aluminium nitride (AlN), diamond, etc., Al_2O_3 is one of the most popularly used inorganic fillers for polymer composites, since they can provide good thermal conductivity, high electrical resistivity and low production cost [14].

High volume fraction of thermally conductive fillers (ϕ_f = 70–80 vol%) are popularly required to achieve high thermal conductivity. Unfortunately, the softness and flexibility essential to conforming surface roughness at the interface of the electronic devices are lost with such large filler content. To achieve those two contradictory goals simultaneously, loading of fillers should be restricted to a low level and methods beyond simple mixing of inorganic fillers and polymer are required. Recently, enhanced thermal conductivity of polymer composites was achieved with plate-like fillers which was uniaxially aligned by applying external field [15–17]. For example, Fujihara et al. applied direct current (DC) electric field to hexagonal BN containing polymer composites [16] and Cho et al. applied extremely high magnetic field (~100 T) to the same composites [17]. However, very large external field is required to carry out large improvement in thermal conductivity of the composites. Recently, Lin et al. successfully oriented plate-like BN fillers in polymer composites simply by applying moderate magnetic field with a pair of conventional permanent magnets [19]. Thus far, most of experimental works have been focused on orientational alignment of plate-like powders to improve their thermal conductivity, since anisotropic magnetic particles undergo rotational force under uniform magnetic field [20–22]. However, application of magnetic field to polymer composites having alignment of morphologically isotropic fillers with rotational symmetry is quite rare. Magnetic interaction between spherical particles with magnetic dipole moments is popularly found in colloidal systems and often induces ordered assembly of particles [23]. In this study, we demonstrated linear clustering of spherical Al_2O_3- Fe_2O_3 particles in polymer composites induced by external magnetic field. The thermal transport properties of polymer composites were dramatically improved by magnetic field even at a low volume fraction of thermally conductive fillers.

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Nomenclature

u_{HS}	Hard sphere interaction potential
μ_0	Magnetic permeability of vacuum
$\boldsymbol{r}_{ij}$	Center-to-center distance of the spherical fillers
d	Diameter of the spherical filler
$\boldsymbol{\mu}_i$	Magnetic dipole moment of the spherical filler
ρ	Density (g/cm^3)
D_T	Thermal diffusivity (mm^2/s)
C_p	Specific heat (J/K)
K	Thermal conductivity (W/K)
M_S	Saturation magnetization (emu/g)
θ	Angle between magnetic field
u_{DD}	Dipole-dipole interaction
Γ	Magnetic coupling factor
ϕ_f	Volume fraction of fillers
g(r)	Radial distribution function
t_m	Characteristic time required for their aggregation under magnetic field
η_r	Viscosity of the colloidal suspension
μ_l	Viscosity of liquid
ϕ_m	Densest possible packing fraction for spherical particles

2. Materials and methods

Spherical Alumina (Al_2O_3, 7 μm, DAW-07) particles were purchased from Denka (Japan) and $FeCl_2$ (99%), urea (99%) and 2-ethyl-4-imidazolium (EIDZ, 99%) were purchased from Sigma-Aldrich (USA). Diglycidyl ether of bisphenol F (DGEBF, YD-170, E.E.W = 167.5 g/eq) was kindly donated by Kukdo chemicals (Korea). Here, EIDZ was used as curing agent for epoxy resin.

2.1. Preparation of Fe_3O_4-decorated Al_2O_3 and polymer composites

3 mmol of $FeCl_2$ and 30 mmol of urea were dissolved in 100 ml of deionized water at room temperature. Subsequently, 20 g of Al_2O_3 particles were introduced to the solution and the mixture was heated to 100 °C with vigorous stirring to precipitate Fe_3O_4 nanoparticles on surface of Al_2O_3 particles. The prepared Al_2O_3-Fe_3O_4 hybrid particles were washed with water and dried in the drying oven at 80 °C overnight.

The prepared Al_2O_3-Fe_3O_4 hybrid particles were mixed with epoxy resin composed of 4: 1 mixture of monomers (DGEBF) and curing agent (EIDZ) using a planetary mixer (ARM-310, Thinky, Japan) with rotating speed of 1700 rpm for 3 min. The prepared mixture was homogenized for 10 min to achieve uniform microstructures and to destroy aggregation of fillers. The polymer mixture was degassed in a vacuum chamber for 1 h and casted with a teflon mold (12 mm (width) x 12 mm (height) x 2 mm (thickness)) to form plate-like specimen. Subsequently, uniform magnetic field of 1500 Oe was applied by arranging casted specimens between a pair of permanent magnets. The magnetic field was maintained for 5 min along out-of-plane direction of specimen before subsequent curing at 80 °C for 1 h in the absence of magnetic field. Sometimes, prolonged exposure to external magnetic field was carried out to check the effect of exposure time on thermal properties of polymer composites.

2.2. Numerical simulation

Alignment of particles under magnetic field was numerically simulated with off-lattice Monte Carlo method [24–27]. Basic sets of simulation consisted of N = 1000 particles and interaction between spherical particles was modelled with combination of magnetic dipole-dipole interaction and hard sphere modification (u_{HS}) [28]:

$$\mathrm{u(i,j)} = u_{HS}(r_{ij}) + \frac{\mu_0}{4\pi}\left(\frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})}{r_{ij}^5}\right)$$

$$u_{HS}(r_{ij}) = \begin{cases} \infty, & r_{ij} \le d \\ 0, & r_{ij} > d \end{cases} \quad (1)$$

where μ_0, $\boldsymbol{r}_{ij}$, d, $\boldsymbol{\mu}_i$ denote the magnetic permeability of vacuum, the center-to-center distance, the diameter, and the magnetic dipole moment of the spherical filler, respectively. The magnetic dipole moment was obtained from magnetic hysteresis data of Al_2O_3-Fe_3O_4 particles. For simplicity, we assumed that spins of all particles were aligned to the same direction of external magnetic field and particles had homogeneity both in composition and in size. Numerical simulation was performed with 10^7 trial moves within a framework of which dimensions were set to be $15d \times 15d \times 10d$. Total energy of system was determined by summation of inter-particle interaction and acceptance of any trial move was determined by classical Metropolis algorithm at temperature of 300 K. Periodic boundary condition was adopted to minimize edge effect [29].

2.3. Characterization

The bulk density (ρ) of the specimens was calculated based on Archimedes' principle. The thermal diffusivity (D_T) was measured at room temperature with disk samples using laser flash method (LFA467, Netzsch Instruments Co.). The specific heat (C_p) was measured with the same instrument by scanning various temperatures from 25 °C to 50 °C using pyroceram 9606 as a standard reference material. C_p of test sample was obtained by comparing properties of test sample of under investigation to known physical properties of reference material from the following equation [30]:

$$C_{p,\,meas} = \frac{\Delta T_{ref}(\rho_{ref} l_{ref}) C_{p,ref}}{\Delta T_{meas}(\rho_{meas} l_{meas})} \quad (2)$$

where △T, l and ρ are temperature change during laser flash, thickness and density, respectively. Here, the subscripts of "ref" and "meas" refer to the reference material and test sample under measurement. The thermal conductivity (K) was calculated with formula: $K = D_T \times C_p \times \rho$. The morphology of Al_2O_3-Fe_3O_4 particles and the microstructure of their polymer composites were checked with field-emission scanning electron microscopy (FE-SEM) with a JEOL 6700F system. To investigate the microstructure of composites, the polymer composite was cut along the direction parallel to magnetic field and polished with emery papers and diamond pastes. Magnetic hysteresis was recorded with a vibrating sample magnetometer of Lakeshore 7400 system. In addition, optical microscopy was done with optical microscope (Eclipse MA200, Nikon) equipped with CCD and images were captured with software. Thin layer of the polymer composite was prepared by dropping uniform mixture of Al_2O_3-Fe_3O_4 particles, monomers and curing agents between two glass cover slips. Magnetic field was applied along in-plane direction of glass plates before curing. Filler loading of the mixture for thin composite layers was set to be 1 vol% and cured at 80 °C for 60 min in drying oven.

3. Results and discussion

3.1. Formation of Al_2O_3-Fe_3O_4 particles and their alignment under external magnetic field

In typical experimental procedure, Fe_3O_4 particles were synthesized from precipitation of Fe^{2+} ions by decomposition of urea which releases NH^{4+} ions at the elevated temperature (*ca.* 90 °C) [31–35]. Formation of Fe_3O_4 particles was confirmed from the X-ray diffraction