Preparation of graphene oxide/polyvinyl alcohol microcomposites and their thermal conducting properties

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ABSTRACT

In this article, we report the fabrication of graphene oxide (GO)/polymer composite structures that may be candidates for use as effective heat dissipation materials. GO was well dispersed in aqueous polyvinyl alcohol (PVA) solutions; anisotropic fiber structures of GO/PVA composites were then prepared by freeze-drying under controlled freezing conditions. GO was well dispersed in the microfiber structures of PVA, and morphologies of the GO/PVA composite structures could be controlled through the concentration of the starting solution, the freezing temperature, freezing rate, and direction of the freeze. Thermal conducting properties were found to depend on the morphology of the composite structures and the content of GO. Anisotropic thermal conductivity was found for some structures.

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1. Introduction

There is tremendous growth in the importance of heat dissipation design because advanced electronic devices employ downscaled circuits that allow significant reductions in device sizes. The accumulation of heat in an enclosure is potentially damaging to electronic components, leading to shorter life expectancy for electrical and electronic devices. Conventional heat dissipation materials are manufactured by introducing highly thermal conductive fillers, such as metal and metal oxide microparticles, into polymer matrices. Polymer composites offer such advantages as lightweight, ease in processing, and high resistance to corrosive environments [1–4]. There is the compatibility issue between filler and matrix materials.

As promising thermal conducting filler materials, carbon materials have been receiving significant attention owing to their high thermal conductivity, low coefficient of thermal expansion (CTE), low density, and high compatibility with polymers [5–8]. Thermal conductivities of single-layer graphene, diamond, and carbon nanotubes at room temperature (RT) are assumed to be up to 5300 W/mK, 2000 W/mK, and 3500 W/mK, respectively. These are very high values compared to common thermally conductive materials, such as Cu (400 W/mK) and Al (250 W/mK). However, despite theoretical estimates for high thermal conductivities of carbon materials, no experimental results have been reported to verify them. For practical applications, such materials must be easy to process, inexpensive to manipulate, offer good compatibility with the matrix material, and so on.

Graphene oxide (GO) derived from graphene is attracting extensive interest in many emerging fields because it can be inexpensively mass produced from graphite by chemical oxidation and exfoliation. In addition, GO that contains a range of reactive oxygen functional groups can be variously modified through chemical functionalization to provide good compatibility with polymer materials. Thus, GO/polymer composites are good candidates for designs of heat-dissipating materials.

To improve the thermal conductivity in dielectric materials, the design of the structure should lead to an increase in the phonon mean-free path. If GO is well dispersed and morphologies of the microcomposite structure can be tailored, the distance related to the phonon effect can be controlled and construction of an effective heat-dissipating system can be expected. In this study, GO/polymer microcomposites with various GO content were prepared by freeze-drying, and the effects of their morphologies and content of GO on thermal conductivity were investigated.
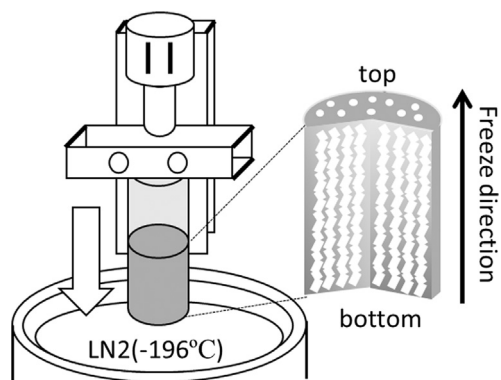
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2. Materials and methods

2.1. Materials

We used PVA (Nacalai Tesque, INC, Kyoto, Japan) with a degree of polymerization of 500 and a degree of saponification of 88%. GO was prepared from natural graphite powder (95%, Wako Pure Chemical Industries Ltd., Osaka, Japan) by a modified Hummers' method [9,10]. The structure of GO was evaluated by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD, Rigaku Rint 2500 HV), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and atomic force microscopy (AFM, Agilent 5500). These evaluations are described in the supplementary data.

### 2.2. Preparation of GO/ PVA composites

GO aqueous dispersion and PVA solution were mixed at various concentration ratios. The GO/PVA solutions were frozen at −23 °C (in a freezer for 12 h) or at −196 °C (by liquid nitrogen, LN2). Shapes of samples, columnar or cubic, were determined by shapes of containers for freeze. The solutions placed in PTFE (0.25 W/mK) or craft paper (0.04 W/mK) containers with bottoms of copper (400 W/mK) were frozen by LN2, and the rate and direction of freezing were controlled by using Z stage as shown in Scheme 1 [11]. The samples were then freeze-dried. After freeze-drying, the GO/PVA composite structures were observed by FE-SEM (Hitachi S-4800).

2.3. Thermal conductivity measurements

Columnar samples with diameters of 1 cm and heights of 1 cm were prepared for thermal conductivity measurements. GO/PVA composites containing 0 wt%, 10 wt%, and 50 wt% GO were labeled GO0, GO10, and GO50, respectively. Samples were placed on a hotplate controlled at 40 °C, and temperature changes were

Scheme 1. Experimental setup for controlled freeze of solution with Z-stage.
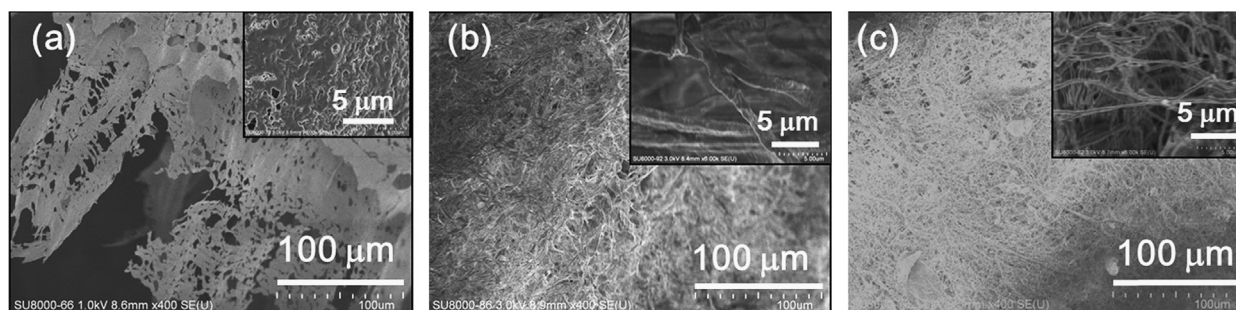
Fig. 1. SEM images of PVA porous structures. 1 wt% PVA solutions were frozen at (a) −23 °C and (b) −196 °C. (c) A 0.2 wt% PVA solution was frozen at −196 °C. These samples were obtained by freeze-drying.
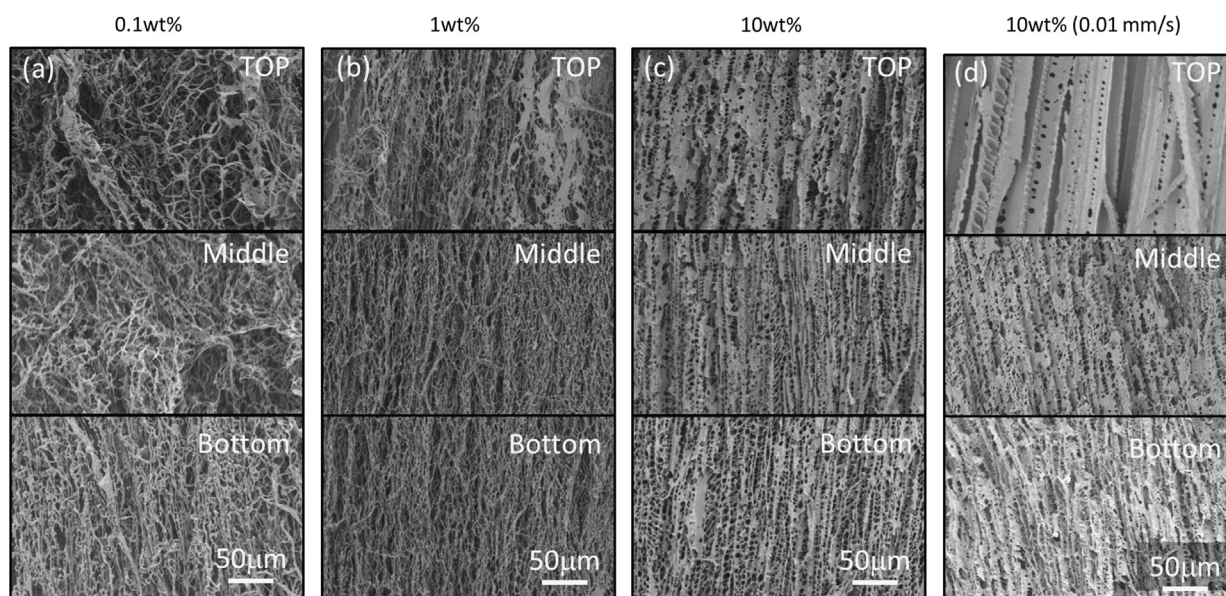
Fig. 2. SEM images of PVA mesoporous structures prepared by freeze-drying. (a) 0.1 wt%, (b) 1 wt%, and (c, d) 10 wt% PVA solutions were frozen at (a–c) 0.1 mm/s and (d) 0.01 mm/s. All these samples were frozen with LN2, with the freezing direction from bottom to top.