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

Sunnam Kim^a, Yuki Azuma^b, Yutaka Kuwahara^{a,c}, Tomonari Ogata^e, Seiji Kurihara^{a,c,d*}

^aGraduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1,

Kumamoto 860-8555, Japan, ^bDepartment of Applied Chemistry & Biochemistry,

^cPHOENICS, ^dJST-CREST, ^eInnovate Collaboration Organization, Kumamoto
University

Tel: +81-96-342-3677, Fax: +81-96-342-3679, E-mail: sn-kim@kumamoto-u.ac.jp

Abstract

In this paper, 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 via 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.

Keywords

Graphene oxide; Polyvinyl alcohol; Polymer microcomposite; Anisotropic thermal conductivity; Fiber structure; Freeze dry

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], [2], [3], and [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], [6], [7], and [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.

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] and [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

PVA solutions containing GO at various concentrations were prepared and frozen at -23°C (in a freezer for 12 h) or at -196°C (by liquid nitrogen, LN2). Solutions frozen by LN2 were placed in PTFE tubes (about 0.25 W/mK) with bottoms of copper (400 W/mK), and the rate and direction of freezing were controlled 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 0wt%, 10wt%, and 50wt% GO were labeled GO0, GO10, and GO50, respectively. Samples were placed on a hotplate controlled at 40°C , and temperature changes were measured using infrared thermography (Thermo Testo 875i). Room temperature before heating was 14°C . The directions of fiber axes for all samples were perpendicular to the plane of the hotplate. In addition, cubic samples ($1.5\text{ cm} \times 1.5\text{ cm} \times 1.5\text{ cm}$) were prepared from GO50, and

temperature changes were measured perpendicular and parallel to the fiber axes on the hotplate controlled at 50°C. Room temperature before heating was 18°C.

3. Results and discussion

Sublimation of water during freeze-drying of polymer aqueous solutions leads to the creation of porous polymer structures. By changing the freezing temperature and concentration of the starting solution, morphologies of the structures can be controlled as shown in Fig. 1. When the 1wt% PVA solution was frozen at -23°C , platelike PVA structures formed (Fig. 1(a)). But when the 1wt% PVA solution was frozen at -196°C by LN₂, network structures formed from fibers as thick as about 2 μm (Fig. 1(b)). The resulting morphology strongly depended on the freeze temperature, and microfiber structures could be obtained using a rapid freeze rate at the lower temperature [12], [13], and [14]. It is assumed that, with a rapid freeze, water crystals corresponding to pores were more homogeneous. For the lower PVA concentration of 0.2wt% frozen by LN₂, the thickness of PVA fibers decreased to about 0.5 μm (Fig. 1(c)). Thickness of the fibers could be controlled by varying the concentration of the PVA solution.

Because the morphology of the composite structure was mainly determined by the

conditions during freezing, control of the freezing direction, freeze rate, and temperature were explored for preparing an oriented microfiber structure. When a 1wt% PVA solution was frozen by LN2 at a freeze rate of 0.1 mm/s, the fibers were aligned in the freezing direction, as shown in Fig. 2. Apparently, crystallization growth of the PVA solution proceeded in the freezing direction. Consequently, an oriented microfiber structure was easily constructed by freeze-drying, and the thickness and orientation of fibers could be controlled.

Fig. 1. SEM images of PVA porous structures. 1wt% PVA solutions were frozen at (a) -23°C and (b) -196°C . (c) A 0.2wt% PVA solution was frozen at -196°C . These samples were obtained by freeze-drying.

Scheme 1. Experimental set-up for controlled freeze of solution with Z-stage.

Fig. 2. SEM images of PVA mesoporous structures prepared by freeze-drying. (a) 0.1wt%, (b) 1wt%, and (c, d) 10wt% 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.

1
2
3
4
5 However, a randomly coiled structure was obtained from a low polymer concentration
6
7
8 of 0.1wt%, despite control of the freezing direction. This might be due to the weak
9
10
11 mechanical strength of thin PVA fibers during drying or by wetting again in the humid
12
13
14 atmosphere. In contrast, for a 10wt% solution, the fiber thickness was larger at the top,
15
16
17 and there was a difference in thickness between the top and bottom; this was especially
18
19
20 true for the slow freeze rate of 0.01 mm/s. This was attributed to changes in
21
22
23 concentration of the solution during the partial freeze process under a controlled freeze
24
25
26 rate; because polymer excluded from water crystals migrated to the unfrozen top, which
27
28
29 led to different polymer densities in the composite along the freezing direction. For low
30
31
32 polymer concentrations of 1wt% and 0.1wt% with a slow freeze rate of 0.01 mm/s, the
33
34
35 composites clearly shrank because of the thin and weak PVA fiber structure at the
36
37
38 bottom where the polymer concentration was lower. Therefore, thermal conductivities
39
40
41 were measured on the GO/PVA composite structure prepared from the 1wt% PVA
42
43
44 solution frozen at 0.1 mm/s.
45
46
47
48
49
50
51
52

53 For the GO/PVA composites, GO0, GO10, and GO50 containing 0wt%, 10wt%, and
54
55
56 50wt% of GO, respectively, about 1 μm of GO was embedded in about 5- μm -thick-PVA
57
58
59
60
61
62
63
64
65

1
2 fibers. The GO was well dispersed in the polymer with good compatibility on the basis
3
4
5 of many functional groups; this was demonstrated by XRD results in which the intrinsic
6
7
8 peak of GO at around 10° ($d = 0.83$ nm) disappeared in GO/PVA composite structures,
9
10
11 as shown in Fig. 3. For a compressed sample of GO50, a broad small peak appeared
12
13
14 around 5° ($d = 1.67$ nm), corresponding to twice the distance of the pristine GO stack
15
16
17 and demonstrating well-dispersed GO with almost a constant distance.
18
19
20
21
22
23

24 The effects of GO content on thermal conductivities of GO/PVA composites were
25
26
27 investigated in the direction of the fiber axes. As shown in Fig. 4(a), GO50 showed
28
29
30 significant temperature increases compared to GO0 and GO10. The rates of temperature
31
32
33 changes for GO0, GO10, and GO50 were estimated to be 0.073, 0.083, and 0.143,
34
35
36 respectively. Furthermore, the anisotropic thermal conductivity of GO50 was evaluated
37
38
39 for directions parallel and perpendicular to the fiber axis. As shown in Fig. 4(b), the
40
41
42 temperature parallel to the fiber axis increased faster than that perpendicular to the axis.
43
44
45 These results demonstrate improvements in thermal conductivity with higher GO
46
47
48 content and thermal anisotropy on the basis of the anisotropic structure of the
49
50
51 composite.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Fig. 3. XRD patterns for GO0, GO10, GO50, and GO.

Fig. 4. (a) Thermal conducting properties of GO0, GO10, GO50, and (b) anisotropic thermal conducting properties of GO50 parallel and perpendicular to the fiber axis.

4. Conclusions

Anisotropic fibrous structures were obtained by freeze-drying under controlled freezing. Morphologies of GO/PVA composite structures were determined by the concentrations of starting solutions, the direction of freezing, freeze rate, and temperature. The thermal conductivity increased as the GO content was increased. An anisotropic GO/PVA composite structure displayed anisotropic values for thermal conductivity.

Acknowledgements

The authors are grateful to partial financial support from JST-CREST, Japan.

References

- [1] Zabihi O, Khodabandeh A, Mostafavi SM. Polym Degrad Stab 2012; 97: 3–13.
- [2] Boudenne A, Ibos L, Fois M, Majeste JC, Gehin E. Compos A 2000; 36: 1545–1554.
- [3] Mamunya YP, Davyenko VV, Pissis P, Lebedev EV. Eur Polym J 2002; 38: 1887–1897.
- [4] Lee ES, Lee SM. J Am Ceram Soc 2008; 91: 1169–1174.
- [5] Chung DDL. App Therm Eng 2001; 21: 1593–1605.

- [6] Balandin AA, Nat Mater, 2011; 10: 569–581.
- [7] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN. Nano Lett 2008; 8: 902–907.
- [8] Mu X, Wu X, Zhang T, Go DB, Luo T. Sci Rep 2014; 4: 3909.
- [9] Hummers WS, Offeman RE. J Am Chem Soc 1958; 80: 1339–1339.
- [10] Tateishi H, Hatakeyama K, Ogata C, Gezuhara K, Kuroda J, Funatsu A, Koinuma M, Taniguchi T, Hayami S, Matsumoto Y. J Electrochem Soc 2013; 160: F1175–F1178.
- [11] Choi WY, Kim HE, Koh YH. J Porous Mater 2013; 20: 701–708.
- [12] Yunoki S, Ikoma T, Monkawa A, Ohta K, Kikuchi M, Sotome S, Shinomiya K, Tanaka J. Mater Lett 2006; 60: 999–1002.
- [13] Gao CY, Wang DY, Shen JC. Polym Adv Technol 2003; 14: 373–379.
- [14] Zhao L, Chang J. J Mater Sci Mater Med 2004; 15: 625–629.

Figure Captions

Fig. 1. SEM images of PVA porous structures. 1wt% PVA solutions were frozen at (a) -23°C and (b) -196°C . (c) A 0.2wt% 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) 0.1wt%, (b) 1wt%, and (c, d) 10wt% 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.

Fig. 3. XRD patterns for GO0, GO10, GO50, and GO.

Fig. 4. (a) Thermal conducting properties of GO0, GO10, GO50, and (b) anisotropic thermal conducting properties of GO50 parallel and perpendicular to the fiber axis.

Scheme 1. Experimental setup for controlled freeze of solution with Z-stage.