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Flexible plane heater: Graphite and carbon nanotube hybrid nanocomposite

Hyeon Ki Park [a], Soo Min Kim [b], Joo Song Lee [b], Ji-Hoon Park [a], Young-Kyu Hong [c], Chan Ho Hong [d], Ki Kang Kim [a,*]

[a] Department of Energy and Materials Engineering and Advanced Energy and Electronic Materials Research Center (AEEMRC), Dongguk University-Seoul, Seoul 100-715, Republic of Korea
[b] Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), San101 Eunha-Ri, Bongdong-Eup, Wanju-Gun, Jeollabuk-Do 565-902, Republic of Korea
[c] Korea Printed Elcetronics Center, Korea Electronics Technology Institute, 111 Banryong-ro, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-844, Republic of Korea
[d] Material Research Team, Dayou Smart Aluminum Co., Ltd., Wanju-gun 565-902, Republic of Korea

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ABSTRACT

We report a facile method for fabricating a flexible plane heater on a plastic substrate using a graphite and carbon nanotube hybrid nanocomposite. To scale up to an industrial level, all the processes are applied in a conventional manner including three-roll calendar and screen printing. Bare graphite flakes are used as a main filler to increase the electrical conductivity of the nanocomposite. To preserve the high crystallinity of graphite, chemical treatments are excluded during the process. A small amount of amino-functionalized multi-walled carbon nanotubes (a-MWCNTs) (10 wt%) are added not only to increase the mechanical strength of the plane heater, but also to improve the heat conduction in the nanocomposite. Therefore, while graphite nanocomposite film mostly peeled off after an adhesion test, a-MWCNT-graphite nanocomposite film adhered on the PET substrate without noticeable change. Furthermore, the fabricated plane heater shows the high performance, compared to that of a graphite nanocomposite, a carbon black/graphite nanocomposite, and Cu wire heaters. We demonstrate that our plane heater is applicable for heating seats of commercial vehicles as well as a flexible plane heater. It will be applied to numerous areas such as heating systems in electrical vehicle and household items for heating.

1. Introduction

The electric plane heater has been extensively used to heat chairs in a vehicle, for winter clothes in the military, and as a heating element in mobile heaters [1,2]. Joule heating ($P = IV = V^2/R$) allows us to conclude that, at a fixed voltage, low resistance is a crucial factor when electrical energy is efficiently converted to thermal energy [3]. Conventionally, metal or metal alloy wires are used as heating materials [4]. However, these type of heaters have limitations in that heating is non-uniform, lifetime can be short on the account of broken wires, and the material is generally heavy [5]. Therefore, other materials and different structures for heaters are desirable in order to overcome these issues. Recently, plane heaters consisting of nanocomposite instead of metals have been introduced. These have the advantage of allowing production at scale with low weight of the devices [6]. However, performance still needs to be improved in terms of reducing the cost, simplifying the fabrication process, and improving electrical conductivity.

Carbon materials, such as carbon black, carbon nanotubes (CNTs), graphite, graphene, or their hybrids, have been used as fillers in nanocomposite to improve electrical conductivity, thermal conductivity, and mechanical strength while also reducing weight [6–11]. Among these carbon materials, carbon black is widely used due to its low cost. However, the percolation threshold for electron conduction compared to that of other carbon materials is high as a result of the large contact resistance between carbon blacks caused by the point contact in the polymer matrix and the low crystallinity of carbon black itself [6]. Therefore, to compensate for the limitations of carbon black, CNTs that offer a high aspect ratio and high crystallinity have been suggested [12–14]. Furthermore, CNTs have a high surface area induce a strong interaction between CNT and polymer. As a consequence, the electrical conductivity, thermal conductivity, and mechanical strength of the nanocomposite are much improved compared to

* Corresponding author. Tel.: +82 2 2260 3955.
E-mail address: kkkim@dongguk.edu (K.K. Kim).

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those of carbon black [15–19]. However, the high cost of CNTs limits their use in real applications.

Graphite flakes are a strong candidate for filler material, among carbon materials, due to the high electrical and thermal conductivity as well as superb mechanical strength caused by a strong sp^2 C—C bond in the layer. In addition, the cost is very low. However, the utilization of graphite flakes in a polymer matrix is difficult due to a weak interaction with the polymer, owing to no reactive functional group existing in the basal plane [20]. As a consequence, these graphite nanocomposites have weak mechanical strength, that is, they are not strong enough for use in heaters. To improve the impregnation of graphite in the polymer matrix, it is necessary to modify graphite to expanded graphite, reduced graphite oxide, or a graphite intercalation compound [10,21,22]. However, the modified graphite had many defects in the basal plane by the chemical treatment, disturbing electron conduction by scattering events in defect sites. Recently, the large area of graphene synthesized by chemical vapor deposition (CVD) has been implemented in transparent and flexible plane heaters [3]. However, fabrication of a large area of the plane heater with current technology such as large-area transfer onto the target substrate is still a challenge.

Recently, hybrid materials such as graphite-CNT and reduced graphite oxide-CNT have been suggested for the synergetic effects [23–30]. Graphite-CNT nanocomposite was adapted to the bipolar plate application. The electrical and thermal properties of the bipolar plate were enhanced by adding the small amount of CNT in the graphite polymer matrix [25]. However, the hot press process at high temperature could not produce the large-area nanocomposite film on flexible substrate. On the other hand, to enhance the mechanical strength of poly(vinyl alcohol) (PVA) composite, reduced graphite oxide-CNT have been used as a filler [31,32]. However, the electrical conductivity of nanocomposite has not been studied. As far as we know, hybrid nanocomposite has not been considered as a flexible plane heater application yet.

In this letter, we introduce a facile method to fabricate a plane heater by using a hybrid nanocomposite based on bare graphite flakes with a small amount of multi-walled CNTs (MWCNT). The polyester as a polymer resin is chosen not only to increase the adhesion between nanocomposite and polyethylene terephthalate (PET) substrate, but also to simplify the coating process. To scale up production to an industrial level, all the conventional processes for fabricating a plane heater are applied, including three-roll calender, screen printing, and package lamination. It should be emphasized that the graphite flakes are not treated with any chemicals in order to retain the high crystallinity of graphite. To disperse the MWCNT, it is functionalized by amino group in the polymer matrix [33–39]. Amino-functionalized MWCNTs (a-MWCNTs) are used not only as a reinforcing agent of the nanocomposite in order to increase the mechanical strength, but also as a heat conduction path in order to improve the performance of the plane heater. The improvement in mechanical strength is confirmed by a standard adhesion test with a cross cut test (ASTM D3359). The effect of a-MWCNT concentration on the graphite-based nanocomposite is further examined. After fabricating the flexible plane heater with graphite/MWCNTs nanocomposite, we found that its performance was better than that of a graphite nanocomposite, a carbon black/graphite nanocomposite and Cu wire heater in terms of the maximum saturated temperature at 0.136 W/cm^2. In addition, the overall weight was lighter by about 20% when compared to the copper wire heater. Finally, we demonstrated that our flexible plane heater can be implemented in real applications, such for heating seats in a vehicle.

2. Experimental

2.1. Sample preparation

To fabricate the plane heater, nanocomposite paste was first produced via dispersion by turbine, three-roll calender, and degassing for removal of the void, as shown in Fig. 1. Then the plane heater on the polyethylene terephthalate (PET) substrate was fabricated by using screen printing followed by lamination with another PET film to complete the plane after the heater fabrication. As-received bare graphite (Hyundai Coma Industry, HC grade) was directly used in this work to preserve the high crystallinity of the graphite. In previous work [42], it was revealed that a-MWCNTs help to improve the interaction between the polymer and MWCNTs and that they assist in forming well-dispersed distribution in the polymer matrix. Therefore, the amino-functionalized MWCNTs were prepared by oxidation, thionyl chloride treatment, and ethylenediamine treatment, and the process is described in

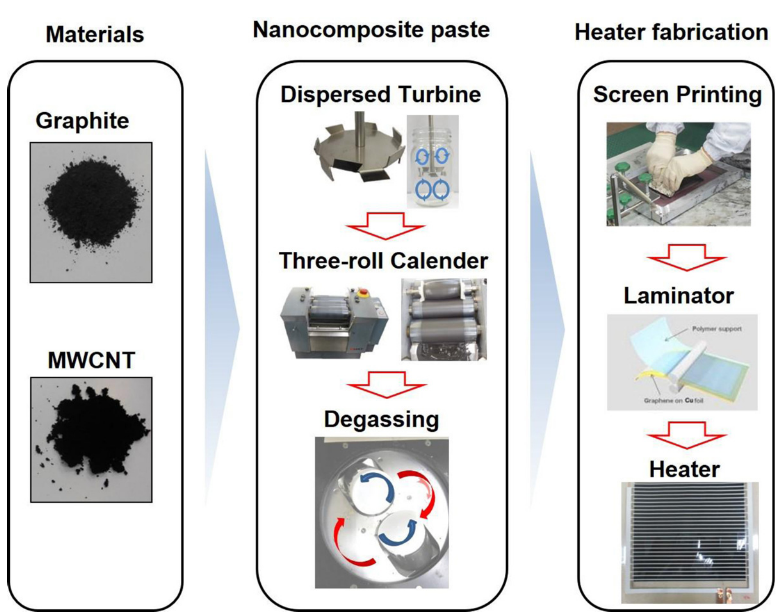

Fig. 1. Schematic diagram of the experimental process: materials, nanocomposite paste, and heater fabrication.