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# Characterization of thermoelectric properties of multifunctional multiscale composites and fiber-reinforced composites for thermal energy harvesting

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## ABSTRACT

We have fabricated two types of multifunctional composites, carbon nanotube (CNT)/glass fiber (GF)/epoxy composites and carbon fiber (CF)/epoxy composites, and evaluated thermoelectric properties of the composites for applications as n/p type thermoelectric materials as well as load carrying structural composites. Several test samples of CNT/GF/epoxy composites with various CNT concentrations were fabricated using a three-roll mill and hand-layup process on a hot plate, while CF/epoxy composite samples were manufactured using a hand-layup process. Experimental results demonstrated that the electrical resistivity of the CNT/GF/epoxy composite (multiscale composite) samples decreased as the CNT concentration increased. In-plane samples showed higher electrical and thermal conductivities due to partial alignment of CNTs in the multiscale composites and continuity of carbon fibers in CF/epoxy composites. Generally, CF/epoxy composites had better electrical and thermal conductivities than those of multiscale composites. In the Seebeck coefficient test, the multiscale composites showed n-type thermoelectric behavior, whereas the CF/epoxy composites showed p-type behavior. When temperature gradients were applied to closed circuits comprised of multiscale composites and CF/epoxy composites as n-type and p-type materials, respectively, an electric current was successfully generated.

## 1. Introduction

Fossil fuel is used in most industries and has become the basis of modern civilization since the industrial revolution. Recently, however, the finite supply of fossil fuel has triggered numerous studies on alternative energy sources. One of the major areas of research on alternative energy is thermal energy harvesting, which converts waste heat to available electric energy [1,2]. Temperature gradient and heat flow are formed in both natural and man-made structures when different temperatures are applied to them, and this provides opportunities for thermal energy harvesting. In the last couple of decades, there has been a dramatic improvement in the performance of thermoelectric materials. Common thermoelectric materials for actual devices are BiTe alloys [3], ReTe alloys [4], BiSbTe alloys [5], $Co_4Sb_{12-x}Te_x$ [6], and $Cu_3BiS_3$ [7,8]. Despite their high efficiency, typical thermoelectric semiconductor materials are expensive, and Te is very toxic and one of the rarest elements on earth as well. Therefore, it is necessary to study new types of materials such as conductive polymer composites or fiber-reinforced composites, which are generally manufactured by simpler processes than semiconductor-based thermoelectric materials and have low manufacturing costs [9].

Zhao et al. [10] reported a comparatively high figure-of-merit in the order of ~0.001 by improving Seebeck coefficient and electrical conductivity simultaneously, while maintaining low thermal conductivity using graphene-MWCNT aerogels. Li et al. [11] showed that the thermoelectric efficiency of polymer-inorganic composites could be enhanced by synthesizing polymers with high Seebeck coefficients. Wang et al. [12] fabricated poly(3-alkylthiophene) (P3AT) and carbon fiber sheet composites to improve thermoelectric properties. They suggested a prospective method for preparing

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large-scale composites with thermoelectricity. Yu et al. [13] fabricated segregated-network carbon nanotube (CNT)/polymer composites and showed that electrical conductivity of the composites could be dramatically increased by creating a network of CNTs in the composite, while the thermal conductivity and thermopower remained relatively insensitive to the filler concentration. Grunlan et al. [14,15] enhanced the thermoelectric properties of carbon nanotube (CNT)-filled polymer composites by modifying junctions between CNTs using PEDOT:PSS. Meng et al. [16] improved the Seebeck coefficient and power factors of carbon nanotube (CNT)/polyaniline (PANI) composites by a wrapping nanostructured PANI coating layer around the CNTs. Hewitt et al. [17] manufactured multilayered fabrics consisting of CNT/PVDF (polyvinylidene fluoride) films and showed that the thermoelectric voltage generated by the fabrics was the sum of the contributions from each layer, resulting in increased power output.

Fig. 1 shows a schematic of a typical structure for a thermal energy harvesting system that has heat source and heat sink for heat absorption and release, respectively [18]. N-type and p-type thermoelectric materials transfer heat from the heat source to the heat sink while generating electric currents [19]. The objective of this research is to develop n-type and p-type thermoelectric materials using carbon nanomaterials, a polymer matrix, and commercial fibers, such as glass fiber and carbon fiber. A three-roll mill and hand-layup process were employed to fabricate composite samples. A special test setup was designed to evaluate the thermoelectric performance of the samples. The electrical conductivity, thermal conductivity, Seebeck coefficient, and figure-of-merit (ZT) of the composite samples were evaluated. The developed composite structures could have multiple applications, including thermal energy harvesting devices as well as load carrying structures.

## 2. Experimental and modeling

### 2.1. Materials

Carbon nanotubes used in this research were multiwall carbon nanotubes (MWCNTs, CM-100) provided by Hanwha Chemical, Korea. Plain-woven glass fiber and carbon fiber (T300-grade) were employed for fiber reinforcement, and both were provided by JMC Co., Korea. The polymer matrix consisted of bisphenol-F type epoxy (YDF-170 from Kukdo Chemical Co., Korea) and a curing agent (SH-101A from Sejin E&C, Korea).

### 2.2. Composite sample preparation

Two types of samples were fabricated and tested: CNT/GF/epoxy multiscale composites and CF/epoxy composites. For the multiscale composite samples, the three constituent materials, pre-determined amounts of CNTs (0.5, 1, 3, 5 wt%), epoxy resin, and curing agent were mixed in a container by manual stirring for 5 min followed by another mixing process using a paste mixer (PDM-300, Dahwa Tech Co., Yongin-si in Korea) (refer to Fig. 2). The revolution and rotation speeds of the paste mixer were 800 rpm and 640 rpm, respectively. The mixture ratio of the epoxy and curing agent was 100:25 by weight, which was the manufacturer-recommended composition. CNTs were dispersed in epoxy resin by a three-roll mill in the following step. The speed ratio of the three rollers was 1:3:9, and the third roller, the fastest roller, rotated at 270 rpm. CNT-epoxy mixtures were passed through the three-roll mill 10 times. After the dispersion process, CNT/GF/epoxy prepregs were prepared. As the first step in prepreg preparation, the CNT-epoxy mixture was poured on a plain-woven GF and then covered with a vacuum bag. The CNT-epoxy mixture was spread on the fabrics by manual pressing. The manufactured prepregs were placed on a hot plate for the hand-layup process and cured with curing and post-curing conditions of 120 °C for 2 h and 150 °C for 2 h, respectively. CF/epoxy composites were also fabricated using prepreg preparation and the hand-layup process. CF/epoxy prepregs were fabricated and cured on a hot plate using the same aforementioned curing and post-curing conditions. A copper plate was attached to each side of the composite sample. Copper plates were placed on top and bottom of impregnated fibers without any adhesives, such as glue, during the hand lay-up process. While being compressed by a vacuum bag, copper plates were fixed through epoxy curing. Since the contact area between copper plate and impregnated woven fibers was large enough and the manufacturing process involved vacuum-induced through-thickness compression, contact resistance was not taken into consideration.

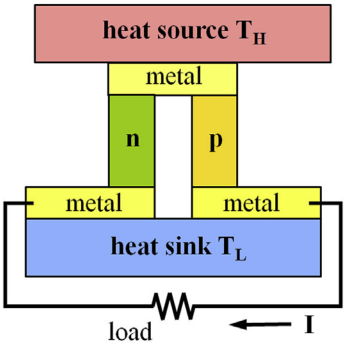

**Fig. 1.** The structure of a thermoelectric system for thermal energy harvesting.

### 2.3. Measurement of thermoelectric properties

#### 2.3.1. Sample geometry

Fig. 3 shows a schematic for measuring voltage difference caused by temperature difference. As shown in Fig. 3(a), two different temperatures are applied to copper sheets on the left and right edges, and in-plane voltage differences were measured. For through-thickness voltage differences (Fig. 3(b)), temperature gradients were obtained by applying different temperatures at the top and bottom of the samples.

Fig. 4 shows sample geometries for the in-plane measurement (Fig. 4(a)) and the through-thickness measurement (Fig. 4(b)). Low and high temperatures were applied to the left and right copper plates on in-plane samples, respectively, and the electronic voltages were measured by a multimeter connected to electric wires of the samples. For through-thickness samples, the temperature gradient was produced by low and high temperatures applied to the upper and lower copper plates of the samples, respectively. Eight layers and sixteen layers of woven fabric prepregs were used to make the in-plane and through-thickness samples, respectively.

#### 2.3.2. Test setup for thermoelectric properties

A special test setup with heating bars was developed in order to set the required temperatures of the composite samples for the characterization of the thermoelectric behavior. A multimeter (Model 2002, Keithley, U.S.A.) was used to measure the voltages created by temperature differences. Fig. 5(a) shows the test setup to measure the thermoelectric properties of the test samples. In-plane test samples were placed between heating bars controlled by the temperature control unit. The electric wires on a sample were connected to the multimeter to measure the voltage. The obtained voltage data were stored on a data collection computer in real time.