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Version Post-print/accepted manuscript

Citation (published version) Sun, Yu-Chen, Daryl Terakita, Alex C. Tseng, and Hani E. Naguib. "Study on the thermoelectric properties of PVDF/MWCNT and PVDF/GNP composite foam." *Smart Materials and Structures* 24, no. 8 (2015): 085034. Doi: 10.1088/0964-1726/24/8/085034

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Study on the thermoelectric properties of PVDF/MWCNT and PVDF/GNP composite foam

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Abstract. Thermoelectric effect is defined as the reversible translation between thermal and electrical energy. In this paper, we investigate the properties of p-type poly(vinylidene fluoride) (PVDF) based polymer composite foams that can be used in next generation energy harvesting applications. The composites were created via continuous melt blending method. Multi-walled carbon nanotubes (MWCNTs) and graphene nano-platelets (GNPs) were used as secondary phases to strengthen the electrical conductivity of the composites. Foam structures were later generated via super-critical carbon dioxide saturation method. We study the material properties between solid and foam samples; the results indicate a dramatic increase in overall thermoelectric properties for GNP foamed samples. We also report at least an order decrease in thermal conductivity which is in favor of thermoelectric effect. An unexpected drop in electrical conductivity was observed after the foaming process and can be explained by large volumetric expansion of the foam. Finally we report the Seebeck coefficient for both types of composite foams: 11 $\mu\text{V/K}$ for 5 wt% MWCNT/PVDF foam and 58 $\mu\text{V/K}$ for 15 wt% GNP/PVDF foam.

1. Introduction

Thermoelectric (TE) effect is known as the direct conversion between electrical and thermal energy and such effect can be explained by three different phenomena: Seebeck effect, Peltier effect, and Thomson effect. When a temperature gradient is applied to a circuit that consists of two different electric conductors, a small current can be observed which is called the Seebeck effect. The opposite phenomenon is called the Peltier effect, of which the junctions of the two conductors may either absorb or release heat when a voltage is supplied to the circuit. Lastly, the Thomson Effect states that when an electric current is passing through a conductor, certain amount of heat (Thomson heat) would be released or absorbed by the material and such heat does not include the non-reversible Joule heating which is generated from the electric resistance nature of the material [1]. Seebeck effect is currently being implemented in various types of temperature sensors or thermocouples [2] while the Peltier effect can be applied in different types of heat engines and coolers [3]. Other than temperature sensors, Seebeck effect also being widely researched for energy harvesting

applications. For example, researchers proposed a few concepts for heat recycling system for car engines [4-6] and possible power sources for space exploration probes [7, 8]. One of the biggest advantages of using TE materials in energy harvesting applications is that no moving component is required in the design and power can be continuous generated as long as the temperature gradient is maintained [9].

Although TE power generation is a promising solution for energy problems, two big challenges remain to be resolved: the low efficiency of power conversion and high material/manufacturing cost [3]. The performance of TE material is defined as figure-of-merit or zT and is expressed in Equation (1)

$$zT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

$S(T)$ is the Seebeck coefficient, $\sigma(T)$ is the electrical conductivity, $\kappa(T)$ is the thermal conductivity, and T is the absolute temperature of which the material is operated in. To simplify the comparison process, z or the “power factor” of TE materials can also be used and is defined as $S^2 \sigma$. As Equation (1) shows, an optimized thermoelectric material should have high Seebeck coefficient and electrical conductivity, but at the same time low thermal conductivity. However, such properties cannot be achieved easily, due to the fact that all three parameters are interrelated, especially the electrical and thermal conductivity are coupled through the Wiedemann-Franz Law [10]. As a result, researchers in the past were primarily focus on semiconductor based materials, such as bismuth telluride (Bi_2Te_3) [11], and antimony telluride (Sb_2Te_3) [12]. Currently, these TE materials have zT close to 1 [13]; to be economically feasible, it was suggested that zT at least 3 would be required [13, 14].

Recently, a new research trend of TE material is emerging, which focuses on flexible and adaptable such as polymer based electric conductive composite materials. Compared to semiconductor materials, polymers have advantages over flexibility, manufacturability, and lower cost. Additionally, polymers are usually known as thermal insulators, which is one of the desired parameters for TE application. Although commonly known as electrical insulators, such properties can be altered when electrically conductive filler are blended into the polymer matrix. The two most widely used conductive fillers currently in the markets are carbon nanotubes (CNTs) and graphene nano-platelets (GNPs). These particles not only have high electrical conductivity (more than 10^5 S/m) [15] but also have high Seebeck coefficient: about 60 $\mu\text{V/K}$ for single walled carbon nanotubes (SWCNTs) and up to 100 $\mu\text{V/K}$ for GNPs [16]. As a result, it was expected that the TE performance of polymer based composites should increase when these particles are blend into the matrix, as demonstrated previously in literature [17].

The current research focus of polymer based TE materials are in the form of thin films and are usually fabricated via solvent or solution casting method [18]. For example, Hewitt et al. presented a TE generator by layering a number of PVDF/multi-walled carbon nanotubes (MWCNTs) thin film in series electrically [19]. Although solvent casting or in situ polymerization are commonly practiced in laboratory scale, manufacturing industries would still prefer the traditional melt blending and continuous fabrication processes due to the simplicity and high production rate.

Other than the electrical conductivity, the thermal conductivity of the material also needs to be controlled in order to further enhance the TE performance. Polymer based materials have two major advantages over semiconductors: the original thermal conductivity of bulk material is often low and small gas bubbles or foam structures can be easily created within the matrix which can further reduce the thermal conductivity [20]. Electrical conductive foam is one of popular research focus. Due to the fact that these foams are constructed from two phase materials, a numbers of different parameters such as filler types, amount of fillers, filler-polymer interaction, and foaming methods/procedures may significantly affect the electrical/thermal properties [21]. In this study, we present the fabrication methods and characterization of novel p-type MWCNT/PVDF and GNP/PVDF electrical conductive foam that can be used in future TE applications. The electrical, thermal conductivity and Seebeck coefficient of both solid and foam samples were investigated.

2. Experimental material and procedure

2.1 Experimental materials

PVDF (Kynar™ 720) was obtained from Arkema Inc. and was used as polymer based matrix for all the samples. The specific gravity of Kynar™ 720 is 1.78g/cm³. Two different types of conductive fillers, MWCNT and GNPs were used in the study. MWCNTs (90% Purity, Nanocyl™ NC7000) were purchased from Nanocyl. The average diameter and length are 9.5nm and 1.5μm. GNPs (90% Purity, Grade 2 Industrial Grade) were purchased from CheapTubes Inc. It has an average thickness of 8nm and average diameter of 2μm as claimed by the supplier.

2.2 Melt blending process

PVDF pellets and both type of fillers were carefully weighted to desired weight percent (wt%): 2, 5, and 8 wt% for MWCNT; 5, 10, 15 wt% for GNP. The particles were first dry mixed and later transferred to melt blending compounder (DSM Xplore micro compounder). The blending conduction was set to 230°C, 50 rpm for 10 minutes for all the composition. The extruded composite strips were water cooled and pelletized.

2.3 Compression molding and shaping

To shape the composite material into desired shapes for testing, the pellets were placed in stainless steel mold and sandwiched between two thin Teflon sheets. Hot press was pre-heated to 230°C for 5 minutes to molten the material. 76 MPa of pressure was then applied for an additional 5 minutes for shaping. The mold was then transfer to water bath for cooling before taking out from the mold. Two different molds were used to fabricate sample with different geometries: disc shape samples (20 mm diameter and 1.2 mm thick) for electrical conductivity testing and small rectangular bar samples (35 by 15 mm and 2mm thick) for Seebeck coefficient measurement. The bar samples were also used in the foaming process.

2.4 Super critical carbon dioxide foaming process

To create the cellular structure within the polymer matrix, super critical carbon dioxide (scCO₂) was used as physical blowing agent and the processes similar to [22] was used. Due to the nature of PVDF, the chamber was preheated to 160°C with 3 different foaming pressures 1000, 2000, and 3000 psi (6.89, 13.79, 20.68 MPa, equivalent) were used to created samples with different foam morphologies. All samples were subjected to 15 minutes of saturation times. Sudden gas release method was used to create the thermal instability within the polymer matrix which results in cellular structure. The chamber was quickly opened and samples were transfer to water bath to solidify the cell structures. Two different types of foam were created: free-expansion foams and mold-controlled foams. The mold thickness was designed to be 2.7 mm in order to fit in the foaming chamber.

3. Experimental characterization methods

3.1 Scanning Electron Microscopy (SEM)

SEM (JSM 6060, JEOL Inc.) pictures were taken for both solid and foam samples to ensure the dispersion of particles and to verify the foam morphology structure. Samples were subjected to brittle fracture after cooled to liquid nitrogen temperature, and then a thin layer of platinum was applied by platinum coating.

3.2 Electrical/Thermal conductivity testing

The electrical and thermal conductivity for both solid and foam samples were measured to verify the TE performance. For electrical conductivity testing, the disc samples were first subjected to 1 minute platinum sputter coating on both side and the edges of the samples were carefully sanded to prevent undesired

conductive path created from the coating. Alpha-N High Resolution Dielectric Analyzer (Novocontrol Technologies) was used to perform the electrical testing. For thermal conductivity measurement, the rectangular bar samples were used and tests were performed by Thermal Constants Analyzer TPS2500S (ThermTest Inc.)

3.3 Seebeck coefficient measurement

A custom made Seebeck coefficient measurement setup was designed that is able to measure both the voltage output and temperature changes simultaneously. The two end of rectangular sample bar was first subject to 2 minutes platinum coating on one single side to create contact electrode for voltage measurement. The sample was then clamped by two set of aluminum blocks on both top and bottom. Each set of blocks contain a small thermocouple sensors (Universal Thermocouple Connector with Type T thermocouple wire, OMEGA Inc.) attached within to measure the temperature difference across the specimen. Masking tape was used to ensure that the only existing electrical pathway is between the sample and the voltage measurement device (Model 2700 Digital Multimeter Data Acquisition and Data Logging System, Keithley Inc.). The sample along with the block sets was then placed vertically on top of a hot plate which was used to create the temperature gradient. While the top part the sample was exposed to room temperature, four different temperature gradient environments was produced, between 10 and 50 K, from the hot plate. The Seebeck coefficient was then calculated by dividing voltage to the temperature difference for each gradient environment.

4. Result and discussion

4.1 Morphological study of particle dispersion and foam structures

4.1.1 Particle dispersion

SEM images were taking to verify the particle dispersion within the polymer matrix. For comparison purpose, SEM images of pure PVDF matrix are shown in Figure 1 while 8 wt% of MWCNT/PVDF and 15 wt% of GNP/PVDF are shown in Figure 2 and Figure 3, respectively. When compared to the pure matrix, all composites figures show ideal particle dispersion within the matrix. Distinct texture can be observed from MWCNT samples with tube lengths approximately 1 μ m. On the other hand, GNP samples show 2D planner structure with area up to few microns. Additionally, a clear alignment can be observed from X2000 images of the 15 wt% GNP/PVDF. Such alignment is likely the result of high pressure compression molding. The 2D structures of GNP can be re-orientated more easily by the high external pressure, therefore filler alignment occurred.

Figure 1 - SEM images of pure PVDF solid sample

Figure 2 - SEM images of 8 wt% MWCNT/PVDF solid sample

Figure 3 - SEM images of 15 wt% GNP/PVDF solid sample

4.1.2 Batch foaming of pure PVDF

PVDF is known as to be a semi-crystalline polymer, which means foam morphology might be harder to control compared amorphous polymer due to the lower gas solubility [23]. Other than nitrogen, researchers also studied the solubility of other gas, such as carbon dioxide and methane [24, 25]. Before foaming the 2-phases composite material, we study three different foaming parameters (gas pressure, temperature, and foaming time). The optimized conditions that produce most intact cell morphology were adapted to foam the composites materials. We found out that pressure has a significant effect for foam structure, as shown in Figure 4. When foaming pressure was low, such as at 1000 psi, not sufficient gas can diffuse into the matrix, which produced smaller cells and thicker cell walls. On the other hand, when a higher pressure (3000 psi) was used, cell wall started to collapse, since high amount of gas wants to rush out after thermal instability was applied. From thesis images, we concluded that the best foaming parameter would be 2000 psi, 160°C and 15 minutes foaming time.

Figure 4 – SEM images of pure PVDF foams (left to right: 1000, 2000, 3000 psi)

4.1.3 Batch foaming of MWCNT/PVDF and GNP/PVDF composite material

Since foaming pressure has significant impact on cell morphologies, different foaming pressure was applied to the composite samples. The same procedures were applied to both the MWCNT/PVDF and GNP/PVDF composites. Due the addition of secondary phase particles, it was unclear how the composite would react to the foaming processes. Recently, Eswaraiyah et al. provided a report on the fabrication of functionalized GNP/PVDF foam using chemical blowing agent [26]. However, the foam has a much thicker cell wall compared to our samples while the thermal conductivity performance of such foam was not specified in the report. To study the composites reaction to the foaming process, different foaming pressures (1000, 2000, and 3000 psi) were used. The SEM images of different wt% MWCNT/PVDF are shown in Figure 5 while GNP/PVDF results are shown in Figure 6.

Figure 5 - SEM images of MWCNT/PVDF foams (up to down: 2, 5, 8 wt%; left to right: 1000, 2000, 3000 psi)

As shown in Figure 5, it is evidential that as the amount of MWCNT added to PVDF increases, a higher gas pressure would be required to foam the composite, which can be observed for samples subjected to 1000 psi foaming pressure. The cell number decreased significantly and no foam was not able to be produced for 8 wt% sample under 1000 psi condition. For lower wt% samples such as 2 and 5 wt%, the cell wall starts to be forced open or ripped if too much pressure, up to 3000 psi, was applied. Such structure may be the result of a large amount of gas being saturated within the matrix. Compared to MWCNT, GNP samples were harder to control, as shown in Figure 6. Such behavior might be the result of likely due to GNPs' 2D structure and large surface area. Again, the amount of particles can affect the morphologies, as shown in 1000 and 2000 psi samples. For samples that contain 15 wt% GNP, extremely large bubbles around 100 µm can be observed. Nevertheless, these bubbles can be minimized if pressure is increased to 3000 psi. Compared to MWCNT samples, 3000 psi is able to produce a more uniform structure for GNPs. As the result, we determined that

2000 psi is the optimized saturation pressure for MWCNT samples while 3000 psi should be used for GNP/PVDF samples.

Figure 6 - SEM images of GNP/PVDF foams (up to down: 5, 10, 15 wt%; left to right: 1000, 2000, 3000 psi)

4.2 Electrical conductivity testing

In order for the composites to inhabit TE effect, the polymer based materials must have certain electrical conductivity. We tested both the solid and foam samples and the results are shown in Figure 7 and Figure 8. According to the literature, MWCNT composites usually have a very low percolation conductivity threshold (approximately 1 wt%) due to its high aspect ratio [27] while GNPs have a slightly higher value, around 5 wt% [28].

Figure 7 – Electrical conductivity of MWCNT/PVDF solid (left) and foam (right) samples

Figure 8 – Electrical conductivity of GNP/PVDF solid (left) and foam (right) samples

The lowest wt% we tested for MWCNT is 2 wt% and 5 wt% for GNP; it is not a surprised to see the both types of composites are highly conductive in its solid state. However, we discovered that the electrical conductivity dropped significantly after foaming while the percolation threshold was increased. For MWCNT samples, the speculating new threshold is between 5 and 8 wt% while for GNP samples the threshold is between 10 and 15 wt%. According to literature, electrical conductivity should only increases while the percolation threshold should decrease [21, 29, 30]. The theory of such behavior is that the bubbles would push the particles into thin cell walls, therefore increasing the chance of particle contact and the formation of electrical pathways. However, such argument does not consider the fact that it is possible a large volume expansion may result in particles being moved away from each other. When the foam is expand in longitude direction, it is possible that such expansion also move the particles to a new location that is further away from its original position, in favor of the expansion direction. In addition, the theory of particle alignment within the cell wall may be applicable if both cell wall and filler are in the same size magnitude, such as extremely thin cell wall with extremely large filler size. If the two parameters do not match each other, such as MWCNTs which are in nanometer scale while the cell wall thickness is in micrometer, the effect of bubble forced reorientation may be very limited. We speculate that such particle reorientation and contact can only happen if both the particles and cell walls are in the same order of size magnitude. The particles we used in this study are simply too small to be affected by the cell morphologies, therefore resulting in the drop of electrical conductivity due to large volumetric expansion.

4.3 Thermal conductivity testing

Similar to the electrical conductivity, the thermal conductivity of both solid and foam samples were measured and are presented in Figure 9. It is not surprised to see that the thermal conductivity of solid samples increase as more fillers are added to the composites. Since gas has extremely poor thermal conduction properties, the CO₂ gas trapped within the polymer matrix can significantly reduce the bulk thermal conductivity.

The idea of creating foam structures within the polymer matrix is to reduce its thermal conductivity in order to improve the TE performance. Similar to the result of electrical conductivity, the thermal conductivity increased along with the wt% in the case of both solid and foam samples. Nevertheless, such increasing trend is almost insignificant for the foam samples when compared to the solid counterparts. Compared to MWCNT, GNP samples have slight higher thermal conductivity at same filler wt%. Such behavior is likely due to the 2D structures of the particles therefore heat transfer occurs more easily.

We also compared the thermal conductive values to the literature and result indicated that melt blending method produces samples with similar thermal behavior when compared to samples fabricated though solvent casting: 0.4 W/mK for 10 wt% single wall carbon nanotube (SWNT)/PVDF reported by Xu et al. [31] and 0.45 W/mK for 0.5, 1, 3, and 4 wt% graphene sheet (GS)/PVDF reported by Yu et al. [32].

Figure 9 – Thermal conductivity of MWCNT/PVDF (left) and GNP/PVDF (right) samples

4.4 Seebeck coefficient measurement

Seebeck coefficient is defined as the voltage produced by a material when temperature gradient is applied to it. The measurement results of different wt% samples are shown in Figure 10. During the measurement, we found out that 2 wt% MWCNT foam and 5, 10 wt% GNP foam samples were not electrically conductive enough for the source meter to pick up the voltage signals. As a result, Seebeck coefficients of these samples were not able to be measured therefore results are omitted. Also, the Seebeck effect of the copper wire (about 1.9 $\mu\text{V/K}$) was taken into account and compensated.

For MWCNT composites samples, foaming slightly reduced the Seebeck coefficient, from 10 to 8 $\mu\text{V/K}$. The foam samples show a decreasing trend in response to the increase of amount of filler content. Such trend was also reported previously in the literature [13]. In addition, all foam samples show a much higher standard deviation compared to solid samples. At 5 wt%, which is very close to the percolation threshold as identified from the electrical conductivity measurement in Figure 7, we obtained reading between 6 to 10 $\mu\text{V/K}$ from different samples. When the filler content increased to 8 wt%, we observed the readings became more stable as the standard deviation also decreased. The similar tendency can be used to explain the Seebeck measurement of 15 wt% GNP/PVDF foams. Measurements were performed on three different samples and the results vary from 25 to 58 $\mu\text{V/K}$, each measurement also accomplish by a large error bar. 15 wt% GNP foam is right on the percolation threshold, therefore measurements may vary significantly and the results depend strongly on the present of any electrical pathway within the samples.

Generally speaking, MWCNT samples have a lower Seebeck coefficient compared to the GNP samples. This variation can be explained by the jump in electrical conductivity, due to the fact that electrical conductivity and Seebeck coefficient are inversely proportional to each other [33, 34]. Since the GNP samples are less electrical conductive than the solid counterpart, only the most excited electron is able to move between the conductive pathways, which result in a higher Seebeck coefficient.

Compared to literature, our MWCNT samples have similar Seebeck coefficients that match previously reported values. Hewitt et al. reported values of 10.05 $\mu\text{V/K}$ for p-type 20 wt% CNT/PVDF thin film samples

[19]. In addition, the sample group reported value close to 30 $\mu\text{V/K}$ for 5 wt% SWCNT/PVDF samples, implied that significant improvement can be achieved by further increasing the aspect ratio of the particles [13]. For the GNP samples, Hewitt et al. fabricated 60 wt% GNP/PVDF thin film with value of 20.3 $\mu\text{V/K}$ via solution casting method [35], while we were able to achieve values up to 25 $\mu\text{V/K}$ by melt blending methods. We also reported an extremely high value for the GNP foam samples, up to 58 $\mu\text{V/K}$. Such value is approximately doubled compared to the solid samples. On the other hand, 15 wt% of GNP filler is right on the percolation threshold, as the measurement results may vary significantly. It is suggest that a higher wt% samples such as 20 wt% would need to be test to validate the actual increase in the Seebeck coefficient.

Figure 10 – Seebeck coefficient of MWCNT/PVDF (left) and GNP/PVDF (right) samples

5. Conclusion

In this study, we present the fabrication methods of 2-phases MWCNT/PVDF and GNP/PVDF composite foams and used a number of methods for characterization. We focus our study on the foam morphologies, electrical, thermal conductivity, and the Seebeck coefficient, since these three parameters are the basic building blocks for TE materials. We report a drop in electrical conductivity after foaming processes which can be explained by volumetric expansion ratio. We are able to lower composites' thermal conductivity by almost an order of magnitude after introduced intact cellular structure into the polymer matrix. Lastly, we report the Seebeck coefficient measurements. Our result indicated that melt blending method is able to provide similar or superior Seebeck coefficient compared to literature. We also demonstrated that the Seebeck coefficient depends strongly on the electrical conductivity, as the measurement value may vary significantly when filler content reaches its electric percolation threshold.

6. Acknowledgment

The authors would like to thank the Natural Science and Engineering Research Council of Canada (NSERC) [Grant number 459389], Canada Foundation for Innovation (CFI) [Grant number 481796], Canada Research Chairs program (CRC) [Grant number 480255] for providing financial support to this research work. Special thanks for Arkema Inc. for providing testing materials.

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