SHAPE MEMORY POLYMER COMPOSITES FOR ENERGY HARVESTING

T.-H. Kang[1], M. Yang[1], S.-Y. Jeon[1], G.S. Lee[1], H.G. Kim[1], S.H. Hong[1], W.–R. Yu[1*]

[1]*Department of Materials science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea*
**woongryu@snu.ac.kr*

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Abstract

As electronic devices become smaller and more efficient, their power consumption has decreased to milliwatts or microwatts scale, justifying the development of a new system for harvesting such small scale power from piezoelectric materials. As such, energy generators with small scale power, for example, a nanogenerator (NG), have attracted much attention. In this study, a new energy harvesting system is developed using shape memory polymer (SMP) and a NG made of zinc oxide (ZnO). Its mechanism is based on the thermal energy, which triggers the shape memory behavior of SMP and is later converted into the electrical energy. The feasibility of developing a new energy harvesting device is systematically investigated focusing on the manufacture of SMP, its composition with ZnO, and the harvesting performance according to the process conditions.

1 Introduction

Due to the global warming and limited petroleum-based energy, green and recycled energies from various sources, e.g., solar cell and nanogenerator (NG), have attracted massive attention [1], even though their actual powers are not comparable to petroleum based energy. Recently, nanogenerators [2], which can convert waste or spare energies generated from environment changes into the electrical energy, have been researched, given that they can provide green energy and their applications become feasible to miniaturized electronic devices. Electronic devices or machines have been optimized in size so that small power from nanogenerators is enough to operate them.

In this study, we combined a piezoelectric material and a shape memory polymer (SMP) into a nanogenerator. SMPs are smart materials that can recover a pre-determined and permanent shape from a temporarily fixed shape upon the application of external stimuli such as heat, pH, light, electric and/or magnetic fields, etc. Furthermore, SMPs shows two-way actuation behavior in a certain condition, i.e., they reversibly actuate upon on-off stimuli. As such SMPs have been utilized to develop smart sensors and products that require repetitive actuation. In the energy aspect, SMPs can convert environmental energy consumed for producing stimuli (e.g., thermal energy) into the mechanical energy [3,4]. This mechanical energy can be used to do a specific work, however, the amount of work, in particular from SMPs, is not enough to operate external devices. To utilize such small mechanical energy, the work needs to be accumulated in other energy form e.g., electrical energy. For this, we utilize a piezoelectric material that can convert the mechanical energy into electrical energy. It is important here to develop a flexible and stretchable piezoelectric system because stiff piezoelectric system can obstruct the deformation of SMPs. Zinc oxide (ZnO) nanowires was chosen for the piezoelectric material, which will be attached to SMP. ZnO features a wurtzite structure without center symmetry, which is the main source of the piezoelectric properties.

In the followings, we discuss an efficient method for preparing flexible ZnO piezoelectric system and two-way SMP sensors, a composition method of the two materials, and characterization of energy harvesting performance of SMP composite.

2 Experimental Section

2.1 Sample preparations

To prepare SMP film, poly(cyclooctene) (PCO, Evonik Industries Vestenamer 8012) and dicumyl peroxide (DCP) (>98% purity, Aldrich) were used as received. PCO (10wt%) and DCP (0.1wt%) were dissolved in toluene and stirred for 24h at 80 ^oC. The solution was dried in hood, obtaining uniformly mixed compounds. The mixture was then pressed at 80℃ for 5 mins under 100 Kgf/cm^2 and cooled to room temperature. Finally, the mixture was cured at 170℃ for 30min under 100 Kgf/cm^2 and again cooled to room temperature.

A poly(propylene) (PP) substrate was selected to manufacture ZnO piezoelectric nanogenerator. The PP substrate was rinsed with acetone, isopropyl alcohol, and deionized (DI) water. A conducting and adhesion chromium (Cr) layer was deposited on the top surface of the PP substrate at a depth of 24 nm. Next, a ZnO seed layer (40nm) was sputtered on the Cr layer. The ZnO nanowires were then synthesized using a hydrothermal process. The surbstrate was immersed in a solution of 0.1M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1M hexamethylenetetramine. The hydrothermal synthesis was carried out in a bath at 85 ^oC for 5h. Gold (Au) layer (10nm) was deposited upon another PP substrate for forming a conducting layer with ZnO nanowires grown on the first PP substrate. Electric wires were attached to two electrodes (Cr and Au conducting layers). SMP film and ZnO piezoelectric nanogenerator were combined using an epoxy adhesive.

2.2 characterizations

The two-way shape memory effect of the PCO film was measured using the following steps [5,6]. Note that the transition temperature of the current SMP is the melting temperature of the soft segments (48 ^oC) of a soft segment. First, the sample was heated to T_h (80 ^oC). Then, a tensile stress (0.4MPa) was applied to the sample. At the constant stress condition, the sample was cooled to T_l (20 ^oC). Under the same constant stress condition, the sample was heated and cooled repetitively, during which the actuating strains were measured. This thermodynamic test was also utilized to investigate how much the mechanical energy results from the two-way actuation of the SMP film.

The electrical properties of ZnO nanogenerator were measured. The substrate on which ZnO nanowires were grown was fixed, while the other substrate with the Au layer was attached to a glass (sliding glass). Simple sliding of the glass bent ZnO nanowires, generating the electrical potential. The potential difference between the two electrode was measured using a electrometer (keithley 6517B).

Lastly, the composite of SMP film/ ZnO nanogenerator was tested to characterize the electrical energy resulting from ZnO nanogenerator, which was induced by the two-way actuation behavior of the SMP film.

3 Results and discussion

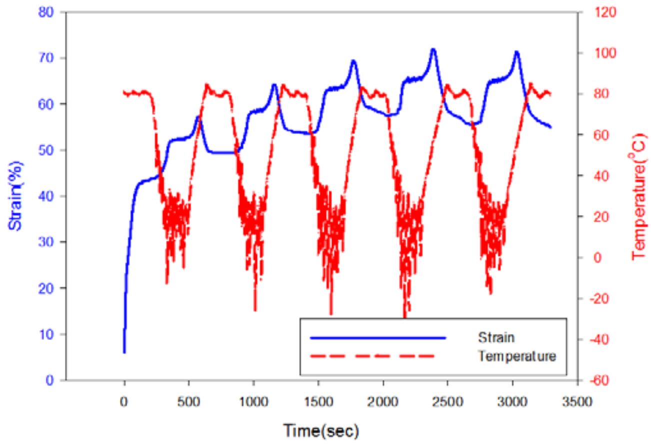

Figure 1. Reversible and spontaneous strain changes according to the cycled temperature

The thermomechanical behavior of the SMP film was characterized. Fig. 2 shows the strain variations of the SMP sample during the thermo-mechanical testing. Under the constant stress condition, the two-way shape memory behavior can be clearly observed according to a cyclic temperature. During the cooling step, the strain increased because the SMP lost its contraction forces and elongated by the constant stress. Interestingly, a deformation lag was observed, i.e., the SMP still expanded in the initial heating stage as temperature increased. It came from the difference between the transition and the softening temperatures of the SMP. The reversible actuation strain was observed to be about 20% when a constant stress of 0.4MPa was applied.

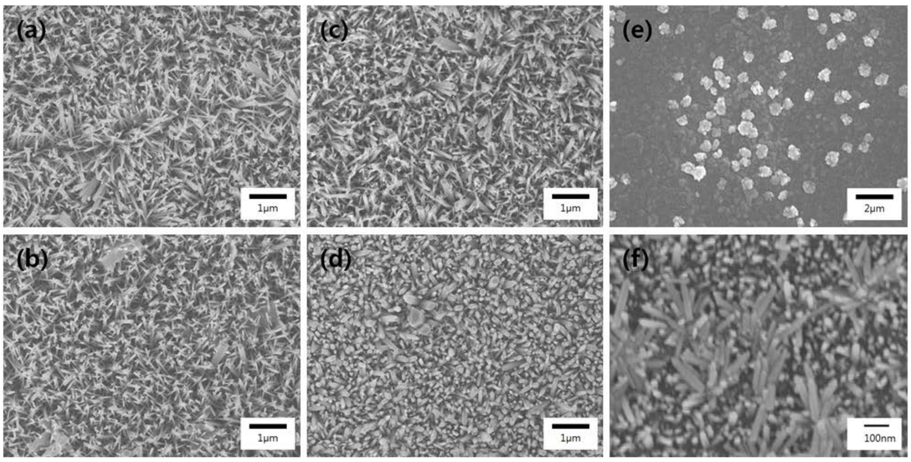

Figure 2. Field-emission scanning electron microscopy (FE-SEM) images of ZnO nanowires grown according to the thickness of Cr layer. a) 6nm, b) 12nm, c) 18nm, d) 24nm. e) surface morphology before hydrothermal method (thickness of Cr layer :18nm), and f) ZnO nanowires grown for 30mins from e).

The morphology of ZnO nanowires was observed using FE-SEM (see Figure 2). The growth of ZnO nanowires was investigated by varying the thickness of the Cr layer. As the Cr layer became thicker, the radius of ZnO nanowires and their density increased. Generally, ZnO grows dominantly at [0001] direction because of the polar effect, allowing vertical growth of ZnO nanowires on the flat substrates. The ZnO nanowires were, however, grown in a slanted manner. This can be explained by the seed particles of ZnO nanowires, which were formed before the hydrothermal method (see Fig. 2 (e)). These particles led to star-shaped and slant nanowires after a short time hydrothermal treatment (30 min). These slant nanowires disturb other wires to grow vertically. Relatively vertical and packed ZnO nanowires were finally manufactured by controlling the layer thickness of sputtered Cr and thus reducing the surface roughness as shown in Fig. 2(d).

ZnO piezoelectric nanogenerator consisted of five layers: a flexible PP substrate, Cr adhesion and conducting layer, ZnO nanowires layer, Au conducting layer, the other flexible PP substrate. When a PP substrare was fixed and the other PP substrate slided, i.e., shear deformation was applied to ZnO nanowires, the electrical potential was recorded as shown in Fig. 3. According to the cyclic sliding behavior (i.e., cyclic shear deformation), the cyclic potential difference was generated in a repetitive manner. This is due to the bent ZnO nanowires by the shearing stress. The measured output varied from 0.02 to 0.05V, implying that the ZnO piezoelectric nanogenerator was properly fabricated in this study.

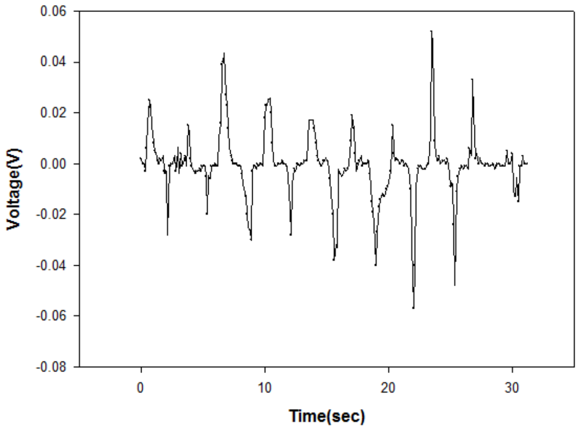

Figure 3. The measured output voltage of the NG

The composites of SMP film and ZnO piezoelectric nanogenerator were prepared and their electrical behavior is under examination. The detailed results and discussion will be presented at the Conference.

4 Conclusion

A cross-linked PCO fim was prepared by hot pressing and thermal curing process and used as a SMP film. It was observed that the PCO film showed two-way actuation behavior by a cyclic temperature variation when an appropriate constant stress was applied and maintained. ZnO piezoelectric nanogenerator was fabricated and tested, showing that the nanogenerator properly generate the potential difference by the shear force applied on the top of the nanowires. The composites of the two elements were fabricated, and their electrical behavior due to a cyclic temperature is under testing. The detailed results will be presented at the Conference.

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