Fabrication of flexible piezoelectric PMN-PT based composite films for energy harvesting

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Abstract

Flexible piezoelectric composite films of lead magnesium niobate and lead titanate (PMN-PT) ceramic and multiwalled carbon nanotube (MW-CNT) in the matrix of polyvinylidene fluoride (PVDF) were fabricated for green energy harvesting and self-powered sensing. Compositions of PMN-PT was varied from 10-50 volume (vol. %) in PVDF matrix while a constant concentration of MW-CNT was maintained (1vol. %). Phase purity of the synthesized composites was confirm by X-ray diffraction (XRD) analysis. PMN-PT powder was found to be in single phase without the presence of any additional peak, which generally arises due to crystallization of another pyrochlore phase. Surface morphology study by scanning electron microscopy (SEM) revealed a well dispersed PMN-PT/CNT in PVDF matrix. The maximum measured output voltage and current during mechanical pressing and releasing conditions were found to be ~ 3 volt and 30 nA, respectively in 30 vol. % PMN-PT composite.

1. Introduction

Extraction and utilization of ubiquitous energy from the environment have been a challenging issue in energy harvesting technology. The most common and accessible renewable energy sources such as solar, wind, thermal and wave can provide the large scale of power. However, for driving the microelectronics devices, wireless sensor networks in healthcare and implantable biomedical devices, etc., milliwatt-scale power should be scavenge from the environment. The harvesting of one such low power energy from mechanical vibrations viz., vibrations from machines, movements in human beings, flow of water, etc., can therefore be a simple and innovative approach. The most common way to generate electrical energy from mechanical vibrations is the use of ceramic piezoelectric actuators made from lead zirconate titanate (PZT), or barium titanate (BTO). However, those monolithic piezoelectric ceramic materials are brittle and hence difficult to integrate in devices. Polymer-ceramic composite materials can combine the flexibility of polymer and the high piezoelectric coupling coefficient of piezoelectric ceramic materials and hence can avoid the breakdown and cracking of the piezoelectric material under stress. Piezoelectric semiconductor like ZnO[1], GaN[2], CdS[3], InN[4], etc., based devices are extensively studied to achieve high performance by fabricating in different processes such as dense nanowire growth, electrospinning and transfer techniques. In order to increase the efficiency and piezo sensitivity, higher piezoelectric symmetry with high mechanical compliant are indeed for energy harvesting. Recently, perovskite based PbZr₆Ti₄O₁₉ (PZT)[5], BaTiO₃[6] and NaNbO₃[7] piezoelectric composites are fabricated on flexible substrates to generate high level of power density. Park et al.[5] have reported carbon nanotube based composites used in PZT-5H and have demonstrated its applications to energize the RGB (Red, Green, Blue) LED (Light emitting diode) arrays and the commercially available seven segment decoder.

Flexible Composites are mostly intend to study for energy harvesting and self-powered sensing due to its improvisation in energy production. Among the commonly used piezoelectric ceramic materials, the lead magnesium niobate and lead titanate (PbMg₁/₃Nb₂/₃O₃ – PbTiO₃), abbreviated as PMT-PT have drawn much attention due its highest piezoelectric coupling coefficient (d₃₃) up to 2500
pm/V which is almost 4 times higher than conventionally used PZT bulk and 30 times higher than BaTiO₃. It has other specific advantages such as negligible hysteresis, lower creep and lack of high voltage as compared to PZT\cite{8}. One can also manipulate the piezoelectric properties by varying the compositional ratio of PMN and PT around the morphotropic phase boundary i.e., PMN-65% and PT-35%. Flexible piezoelectric PMN-PT nanowires based device has produced very large output voltage and current as compared to BaTiO₃ nanoparticle and NaNbO₃ nanowires based devices \cite{9}. So by reviewing the different kind of fabrication techniques and procedures, we are focused on fabrication of flexible composite which is made up of PMN-PT ceramic particles and commercially available multiwalled carbon nanotube (MW-CNT) as organic nanofiller in a polymeric matrix such as Polyvinylidene fluoride (PVDF). MW-CNT organic filler is commonly used in polymeric nanocomposites in order to achieve good mechanical, thermal and electroactive properties because of its low mass density and large aspect ratio and hence chosen as an energy improviser in composites. The important role of the MW-CNTs in these composites is to enhance the stress transfer from the polymer to the PMN-PT particle.

2. Experimental
a) Synthesis of PMN-PT
The PMN-PT powder was synthesized by solid state route via columbite method \cite{10}, Fig.1(a). The commercially available powders MgO and Nb₂O₃ were first stoichiometrically mixed in a roller point mill (Model.No-Secor142(B)) with high purity Yttria-stabilized zirconia (YSZ) balls in Isopropanol medium for 24 h. The ball to powder ratio was 4:1. After that it was dried and calcined at 950°C for 4 h. The calcined powders were then crushed and again ball milled with high purity Yttria-stabilized zirconia (YSZ) balls in Isopropanol medium for 24 h. Then the powder was compacted using a hydraulic press at a pressure of 2 MPa and pellets of 10 mm diameter was made. The pellets were then sintered at 1250°C for 4 h to form MgNb₂O₆. The pellet was then crushed and mixed with TiO₂ and PbO in stoichiometric ratio for synthesis of 0.65 (PMN) and 0.35 (PT). Then the above procedure, i.e, ball milling-calcination-ball milling-sintering, was repeated to form the final PMN-PT product.

b) Synthesis of PMN-PT/CNT/PVDF composite
The composites were prepared via solution casting route, Fig.1(b). The synthesized PMN-PT powder (10, 20, 30, 40, 50 vol. %) was mixed with commercially available MW-CNT powder (1 vol. %). The mixture was stirred in ethanol and water for ~1 h by using magnetic stirrer and then dried up at 80 °C. Again it was stirred in Acetone and a surfactant (span 80) for 24 h and dried at 80 °C. The PVDF solution was made by adding calculated amount of Polyvinylidene fluoride (PVDF) powder in dimethylformamide (DMF) solvent (in the ratio of 1:10 w/w) with continuous stirring in a magnetic stirrer and heating at 85 °C. The dried mixture of PMN-PT/CNT powder was then mixed with PVDF solution by magnetic stirrer. The final PMN-PT, CNT and PVDF well mixed slurry was casted on to a Petri dish and allowed to harden at 85 °C. The dried PMN-PT/CNT/PVDF with approximate dimension of 10 cm diameter was peeled off from the Petridish. This flexi layer was taken as the final composite.

c) Characterizations
X-Ray diffraction (XRD) patterns of the synthesized ceramic powders as well as polymer composites were recorded using Bruker Advance D8 by employing CuKα radiation. The microstructure was studied by Scanning electron microscope (Zeiss Gemini SEM) and energy dispersive X-ray (EDX) analysis. The composites were cut into 1.5 cm x 1.5 cm and were painted with silver paste on both sides that served as electrodes. The connecting wires were connected to the top and bottom electrodes and the whole assembly was sandwiched between laminate pouch and then hot rolled to measure the electrical outputs. The film was repeatedly pressed and released to measure the generated output voltage and current using Keithley Source meter 2410.
3. Results and Discussion

3.1. Structural and Microstructural Analysis

The X-Ray Diffraction pattern of synthesized PMN-PT/CNT/PVDF composites with varying (10-50) vol. % of PMN-PT are shown in Fig. 2. The peaks marked with star correspond to PVDF and is observed in 10 vol.% PMN-PT/CNT/PVDF composite due to higher concentration of polymer. However, with the increase in vol. % of PMN-PT only PMN-PT peaks are observed and the PVDF peaks have disappeared due to the dominance of ceramic content.

The SEM micrographs of the composites as shown in Fig. 3 reveal the presence of both the polymer phase as well as the ceramic phase. The composites with 10 vol.% and 30 vol.% PMN-PT content, Fig. 3. (a) and (b), show uniform dispersion of ceramic in the polymer matrix. However, for 50 vol.% PMN-PT, Fig. 3 (c), particle-particle agglomeration takes place due to higher volume fraction of ceramics. Fig. 3(d) shows the crosssectional view of 30 vol.% PMN-PT composite from which the average thickness is found to be ~70 µm.

![Figure 1. (a) Schematic for synthesis of PMN-PT.](image1)

![Figure 1. (b) Schematic for synthesis of PMN-PT/CNT/PVDF.](image2)

![Figure 2. XRD patterns of PMN-PT/CNT/PVDF composites with varying vol.% of PMN-PT.](image3)

![Figure 3. SEM images of (a) 10 vol.% (b) 30 vol.% (c) 50 vol.% PMN-PT/CNT/PVDF (d) crosssectional view of film.](image4)
3.2. Output Voltage and Output Current

The typical voltage generation graphs, shown in Fig. 4 are obtained on a 3 cm × 3 cm sample area, by manually finger tapping which depicts the real life energy harvesting. The 10 vol.% PMN-PT content composite generates an output voltage of around 1 V, Fig. 4(b). With the increase in PMN-PT content to 20 vol.%, the composite generates an output voltage of around 2 V and is shown Fig. 4(c). The 30 vol.% PMN-PT content composite, Fig. 4(d), shows the maximum output voltage of ~4 V, which is sufficient to light a commercial LED. The generated output voltages decrease with further increase in PMN-PT content and is found to be in the range of 1-2 V for 40 and 50 vol.% PMN-PT, Fig. 4 e-f. This may be due to agglomeration, as revealed from the SEM micrographs, of ceramics in the polymer composite.

Figure 4. (a) Schematic representation of tapping or applying pressure on sample leading to output voltage generation. Output voltage signal under periodic tapping generated in (b) 10 vol.% (c) 20 vol.% (d) 30 vol.% (e) 40 vol.% (f) 50 vol.% PMN-PT composites.

The output current of all the synthesized composites are shown in Fig. 5 which demonstrates an increase in output current with the increase in ceramic content upto 30 vol.% PMN-PT and then decreases with further addition of ceramics. The 10 vol.% PMN-PT composite generates an output current around 5 nA. The slight increase in magnitude of current is observed in 20 vol.% PMN-PT composite with a maximum magnitude of ~10 nA. However, an improvement in output current is clearly seen in 30 vol.% PMN-PT composite, Fig. 4(d), with a maximum value of ~30 nA. With further increase in reinforcement of ceramic particles to 40 and 50 vol.% PMN-PT in composites, the maximum output current shows a decrement and the magnitudes are found to be around 15-20 nA as shown in Fig. 5 e-f. This is ascribed to the fact that agglomeration of ceramic particles, as revealed from SEM micrograph in Fig. 3(c), might have contributed to poor distribution of ceramic particles in the polymer matrix.
Figure 5. (a) Schematic representation of tapping or applying pressure on sample leading to output voltage generation. Output voltage signal under periodic tapping generated in (b) 10 vol.% (c) 20 vol.% (d) 30 vol.% (e) 40 vol.% (f) 50 vol.% PMN-PT composites.

4. Conclusions
A pyrochlore free PMN-PT and CNT based piezoelectric flexible composite films for energy harvesting has been fabricated. The investigation of the output voltage and current reveals that the 30 vol.% PMN-PT/CNT/PVDF composite has the highest output voltage and current with a maximum magnitude ~4 V and 30 nA, respectively. This output voltage and current is comparable with other reported flexible piezoelectric composites. Hence, this flexible composite fabricated with easy technique can be a promising candidate for energy harvesting.

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