Gd5Si4-PVDF nanocomposite films and their potential for triboelectric energy harvesting applications

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Abstract
The triboelectric energy generators prepared using the combination of self-polarized, high beta-phase nanocomposite films of Gd5Si4-PVDF and polyamide-6 (PA-6) films have generated significantly higher voltage of 425 V, short-circuit current density of 30 mA/m² and a charge density of similar to 116.7 C/m² as compared to corresponding values of 300 V, 30 mA/m² and 94.7 µC/m², respectively for the pristine PVDF-(PA-6) combination. The magnetic measurements of the Gd5Si4-PVDF films display a ferromagnetic behavior as compared to diamagnetic nature of pristine PVDF. The presence of magnetic nanoparticles in the polymeric matrix allows for some control over the microstructural properties during the preparation process. The results open new routes for multiferroic composite films to be suitable for multifunctional magnetic and triboelectric energy harvesting applications.

Keywords
Multiferroics, Nanoparticles, Nanocomposites, Polymers, Energy harvester, Nanomagnetism, Differential scanning calorimetry

Disciplines
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ABSTRACT

The triboelectric energy generators prepared using the combination of self-polarized, high β-phase nanocomposite films of Gd$_5$Si$_4$-PVDF and polyamide-6 (PA-6) films have generated significantly higher voltage of ~425 V, short-circuit current density of ~30 mA/m$^2$ and a charge density of ~116.7 µC/m$^2$ as compared to corresponding values of ~300 V, 30 mA/m$^2$ and 94.7 µC/m$^2$, respectively for the pristine PVDF-(PA-6) combination. The magnetic measurements of the Gd$_5$Si$_4$-PVDF films display a ferromagnetic behavior as compared to diamagnetic nature of pristine PVDF. The presence of magnetic nanoparticles in the polymeric matrix allows for some control over the microstructural properties during the preparation process. The results open new routes for multiferroic composite films to be suitable for multi-functional magnetic and triboelectric energy harvesting applications.

INTRODUCTION

Recently, triboelectric generators (TEGs) have garnered much attention due to their high power output and conversion efficiency at a low production cost. TEGs operate by accumulating static charge on the surfaces of different dielectric materials when they are brought into frictional contact with each other, which is then passed onto the external load via electrostatic induction using back electrodes. In order to improve the energy density of TEGs, the dielectric materials should be diametrically opposite in their ability to provide or receive electrons in the triboelectric exchange i.e., one of the materials should lose electrons easily while the other readily accepts electrons. Considering the triboelectric series, it can be observed that a triboelectric positive material such as polyamide-6 (PA6, Nylon) loses electrons when it is in contact with triboelectric negative polymer such as poly(vinylidene fluoride), PVDF, which has a significant ability to gain electrons due to the high electronegativity of the fluorine groups. As such, dielectric-dielectric TEGs based on the combination of fluorinated polymers and polyamides have been shown extensively.

In this work, a TEG was prepared using the combination of tribo-negative Gd$_5$Si$_4$-PVDF and tribo-positive PA-6 films using a facile phase-inversion method. The fabricated Gd$_5$Si$_4$-PVDF TEGs...
showed significantly higher voltage of \(\sim 425\) V, short-circuit current density of \(\sim 30\) mA/m\(^2\) and a charge density of \(\sim 116.7\) µC/cm\(^2\) as compared to corresponding values of \(\sim 300\) V, 30 mA/m\(^2\) and 94.7 µC/cm\(^2\), respectively for the pristine PVDF-(PA-6) combination. The increase in the electrical output for the Gd\(_5\)Si\(_4\)-PVDF/PA-6 TEG system is attributed to the enhanced polarisation and \(\beta\)-phase content of the Gd\(_5\)Si\(_4\)-PVDF films. The work thus introduces a simple route for enhancing the polarisation and power output of TEGs without relying on prior charge injection technique and thus has the potential to be utilised further to making self-powered systems.

**PREPARATION OF Gd\(_5\)Si\(_4\)-PVDF COMPOSITE FILMS AND ASSEMBLING OF TEG DEVICES**

The synthesis of Gd\(_5\)Si\(_4\) nanoparticles has been mentioned in detail elsewhere.\(^6\) The Gd\(_5\)Si\(_4\)-PVDF films were fabricated using a facile phase-inversion process. Further details of the process can be found in our earlier works.\(^6,11–13\) During the quenching process, the Si substrate rested on a N50 neodymium iron boron permanent magnet, which provided a magnetic field that aligned the nanoparticles. The triboelectric counter surface films of polyamide-6 were synthesized using a 20 wt% dope solution of polyamide-6 in formic acid prepared via heating to 70 °C under vigorous magnetic stirring. The spin coating and phase inversion parameters for PA-6 membranes can be found in our earlier works.\(^6,10\)

The 2 cm x 2 cm vertical contact mode TEG was assembled on an acrylic base wherein the first layer of PA-6 film is attached using a conductive adhesive aluminium tape electrode. For the opposite side, either pristine PVDF or Gd\(_5\)Si\(_4\)-PVDF composite films were attached using conductive aluminium tape. These two substrates were then connected using two arc-shaped polyimide supports acting as spacers to maintain the desired spacing between them as shown in Fig. 1.

**CHARACTERIZATION**

The as-prepared Gd\(_5\)Si\(_4\) nanoparticle powders and the composite Gd\(_5\)Si\(_4\)-PVDF nanocomposite films were analyzed for their morphology using scanning electron microscopy and reported elsewhere.\(^3,14\) The vibrational characteristics of the PVDF, Gd\(_5\)Si\(_4\)-PVDF and PA-6 films were examined by FTIR spectroscopy (Thermo Scientific IS10 Nicolet) wherein the spectra were recorded at a nominal resolution of \(\pm 1\) cm\(^{-1}\) for a total of 64 scans. The calculation of \(\beta\)-phase content was carried out using vendor provided OMNIC software. Further characterization of the phase-inversion films was carried out using differential scanning calorimetry (DSC), to investigate the crystalline phase content using a TA Instruments DSC Q2000. The samples, approximate weight 2 mg, were heated at 10 °C/min from 20 °C to 200 °C under 50 ml/min \(N_2\) flow to assess their melting and crystalline behavior. The magnetic properties of the films were investigated using vibrating sample magnetometry in a Quantum Design Versalab. The electrical measurements of the TEG devices were carried out using a dynamic fatigue tester (Powil model YPS-1) in conjunction with a Tektronix MDO3022 oscilloscope and a Keysight B2981A picoammeter. The fatigue tester operates at various adjustable frequencies and loads between 1-1000 N and allows for precise control over the impact load and frequencies.

**RESULTS AND DISCUSSION**

The presence of Gd\(_5\)Si\(_4\) in the composite membranes was confirmed using X-ray photoelectron spectroscopy in the wide energy survey as well as core level scans (Fig. 2(a, b)). The core level Gd4d and Si2p spectra for the Gd\(_5\)Si\(_4\)-PVDF films confirmed the presence of magnetic Gd\(_5\)Si\(_4\) particles in the matrix.

The DSC thermograms for the pristine PVDF and Gd\(_5\)Si\(_4\) composite films shown in Fig. 2(c) provides evidence of the increase in the crystalline \(\beta\)-phase upon the addition of Gd\(_5\)Si\(_4\) nanoparticles. The melting temperature, T\(_M\), for the starting PVDF pellets and pristine PVDF membranes is in the range of 172-173 °C, with a slightly lower value for PVDF membranes. Upon the addition of Gd\(_5\)Si\(_4\) nanoparticles to PVDF matrix, the T\(_M\) of the composite films shows a significant reduction to \(\sim 170\) °C, with shoulder-like structures appearing at both low and high temperature regions. While there is ongoing debate on the exact melting temperatures of the various crystalline phases of PVDF, it is largely accepted that the \(\beta\)-phase melting occurs in the range 165–170 °C; \(\alpha\)-phase crystals in the range 172–175 °C with the \(\gamma\)-phase melting between 175 and 180 °C (marked in Fig. 3(a)).\(^16-12\) Considering the thermograms shown in Fig. 2(c), it can be observed that for the composite Gd\(_5\)Si\(_4\)-PVDF membranes, they are largely enclosed within the range of the 165-170° C, corresponding to the dominant \(\beta\)-phase. In fact, the T\(_M\) of the Gd\(_5\)Si\(_4\)-PVDF films is nearly 166.8° C, which is approximately 3.0-5.0 °C lower as compared to that of pristine PVDF membranes and pellets, thus confirming that the lowering of the T\(_M\) can be attributed to the enhanced \(\beta\)-phase content of the films. The addition of Gd\(_5\)Si\(_4\) nanoparticles to the PVDF matrix clearly leads to an increase in the crystallinity wherein the ΔC\(_E\) increased from \(\sim 38.6\)°C for the PVDF pellets to approx. 46.8° (for pristine PVDF films) to nearly 62.0% for the 5wt% Gd\(_5\)Si\(_4\)-PVDF films calculated from the literature.\(^10-12\) Since both
the pristine and Gd$_5$Si$_4$ membranes were prepared using the phase inversion process, while the slow liquid-liquid de-mixing of DMF and deionised water provides longer crystallisation times, the nucleation effects provided by the Gd$_5$Si$_4$ nanoparticles are believed to be responsible for the significant enhancement of the crystalline phase.$^{10,12,13}$

The FTIR spectra of the PVDF pellets, pristine PVDF and Gd$_5$Si$_4$-PVDF composite membranes is shown in Fig. 2(d) wherein the quantification of the piezoelectric $\beta$-phase relative to the $\alpha$-phase was carried out using the signature vibrational bands at 840 cm$^{-1}$ (CH$_2$ rocking Magnetic field (kOe) and CF$_2$ asymmetric stretching vibration) and 760 cm$^{-1}$ (CF$_2$ bending and skeletal bending), respectively.$^{6,10-12}$ It can be observed that upon phase inversion, a significant increase in the $\beta$-phase is observed for the PVDF membranes, wherein the $\beta$-phase is enhanced to $\sim$49% from an initial value of $\sim$39% for the starting PVDF pellets. With the introduction of Gd$_5$Si$_4$ nanoparticles, under the same processing conditions, the $\beta$-phase is further enhanced to $\sim$79%. The values obtained in this work are very similar to our earlier reported works.$^{14}$

Fig. 3 shows the measurement of magnetization vs. temperature in the range of 200-380 K and at an applied field of 100 Oe. While the pristine PVDF films show a diamagnetic behavior; the nanocomposite Gd$_5$Si$_4$-PVDF films were ferromagnetic below 310K and showed a transition around this temperature. Inset of Fig. 3 shows the hysteresis measurement at room temperature wherein it can be clearly seen that the films are ferromagnetic at room temperature with negligible coercivity. The ferromagnetic behavior of the film is attributed the presence of Gd$_5$Si$_4$ nanoparticles in the composite film wherein the diamagnetic behavior of the pristine PVDF film is overcome by the large magnetic moment of ferromagnetic Gd$_5$Si$_4$ nanoparticles.
TEG ELECTRICAL TESTING

The TEGs fabricated with the Gd$_5$Si$_4$ nanocomposite films and pristine PVDF (as reference) was tested for their triboelectric output using a dynamic fatigue tester. The intrinsic output characteristics of open-circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$), of TEGs were measured to represent the electrical output of the TEGs. Voltage measurements were taken at impact forces ranging from 20-80 N at a constant frequency of 5 Hz and a spacer distance of 8 cm. As illustrated in Fig. 4 (a and b), the voltage response of both Gd$_5$Si$_4$-PVDF and pristine PVDF TEGs increases almost linearly with the applied force. Moreover, it was observed that the average peak-to-peak $V_{oc}$ of the Gd$_5$Si$_4$-PVDF TEG (~200 V) at 20 N impact force condition is around 1.3 times greater than the peak-to-peak $V_{oc}$ of pristine PVDF (~150 V) tested at the same conditions. With the increase in the force, the variation of the outputs from the two devices increased to ~1.5 times across the range, with maximum Voc values of 425 V and 350 V for Gd$_5$Si$_4$-PVDF TEG and pristine PVDF TEG, respectively.

From the above equation, it can be clearly observed that the $V_{oc}$ is directly proportional to the spacer distance and the surface charge density (see Fig. 4(b) inset for the variation of the output $V_{oc}$ at two different spacer values). This variation in the $V_{oc}$ can also be explained considering the mechanical and elastic properties of the porous PA6 and Gd$_5$Si$_4$-PVDF membranes, wherein an increase in the impact force causes a larger interfacial deformation and filling of the vacant pores, leading to a larger effective contact charging area and therefore higher surface charge density and thus higher open circuit voltage.

Considering the short circuit current density curves shown in Fig. 4, at low impact conditions (20-60 N), the observed current density from the Gd$_5$Si$_4$-PVDF TEG was ~5 mA/m$^2$ lower than the values observed from the pristine PVDF TEG. However, with the increase in the impact force to 80N, a rapid increase in the $J_{sc}$ was observed wherein the current density values reached almost the same level as that of the pristine TEGs.

![FIG. 3. Magnetization vs. Temperature at an applied field of 100Oe of Gd$_5$Si$_4$-PVDF films. inset Magnetization vs. magnetic field at room temperature. Note, the hysteresis graph doesn’t show observable coercivity.](image-url)

![FIG. 4. TEG electrical characteristics of open-circuit voltage values for (a) pristine PVDF TEG and (b) Gd$_5$Si$_4$-PVDF TEG; short circuit current density of (c) pristine PVDF-TEG and (d) Gd$_5$Si$_4$-PVDF TEG. The inset of (b) shows the variation of the $V_{oc}$ as a function of spacer distance for a 40 N impact force.](image-url)
densities were consistently observed to be higher for the Gd$_5$Si$_4$-PVDF films than compared to the pristine PVDF TEGs. Typically, at lower force values (20, 40N), the calculated charge densities for the pristine and Gd$_5$Si$_4$-PVDF TEG systems were $\sim$37.5 and 60.0 $\mu$C/m$^2$, respectively which upon increase in the force to 80N were enhanced and 116.7 $\mu$C/m$^2$, respectively. This increase in the charge density can be attributed to the nucleation effects provided by the Gd$_5$Si$_4$ nanoparticles leading to the enhanced $\beta$-phase and crystallinity.

Fig. 5 shows the voltage response of the Gd$_5$Si$_4$-PVDF TEG as functions of impact frequency (1-9 Hz) at the fixed working conditions of $\sim$40 N impact force and 4 cm spacer distance. It is obvious that the electrical output values of the Gd$_5$Si$_4$-PVDF are almost proportional to the growth of the working frequency at low working frequency condition (1 to 5 Hz), wherein the $V_{oc}$ increased from approximately 25 V to 175 V with the corresponding increase in $J_{sc}$ from approximately 0.9 mA/m$^2$ to 18 mA/m$^2$. As the working frequency was increased from 5 Hz to 9 Hz, no significant increase in output voltage could be observed; correspondingly, the increase in the current density across this range also slowed down sharply, which could be due to the insufficient contact and transmission of force at higher frequencies. To confirm the mechanical stability of TEG fabricated by Gd$_5$Si$_4$-PVDF film, a stability test was performed by operating the TEG at the working condition of 5 Hz frequency, 4 cm spacer distance and 80 N impact force for 10,000 cycles. By observing the test results shown in Fig. 5(c), the TEG device displayed a stable power generation performance for long-duration operation. The output voltage was maintained around 400 V without any visible attenuation. It should be mentioned that the peak values of $V_{oc}$ measured in the period around 4000 cycles arbitrarily increased to approximately 450 V and slowly decreased to approximately 400 V within 4,000 operation cycles. Thus, the enhanced output from the Gd$_5$Si$_4$-PVDF based TEG device is largely stable, making it useful for applications in energy harvesting from low-medium frequency impact applications.

CONCLUSIONS

Triboelectric nanogenerators were fabricated from aligned Gd$_5$Si$_4$-PVDF nanocomposites. Gd$_5$Si$_4$-PVDF films were synthesized by phase-inversion technique in the presence of an external magnetic field that aligned the magnetic Gd$_5$Si$_4$ nanoparticles during spin-coating process. These aligned films Gd$_5$Si$_4$-PVDF showed significantly higher crystallinity and increased $\beta$-phase fraction as compared to the pristine PVDF films. The assembled TEGs using Gd$_5$Si$_4$-PVDF films against a PA-6 counter material was shown to provide $V_{oc}$ values of $\sim$425V, short circuit current density of $\sim$30 mA/m$^2$ and a charge density of $\sim$116.7 $\mu$C/m$^2$ as compared to corresponding $\sim$300 V, 30 mA/m$^2$ and 94.7 $\mu$C/m$^2$, respectively for the pristine PVDF-(PA-6) combination. The higher values of $V_{oc}$ and more importantly the charge density show the beneficial effects of the addition of Gd$_5$Si$_4$ nanoparticles to the PVDF matrix in enhancing the polarization of the nanocomposites and providing routes for controlling the crystallization and formation of the piezoelectric $\beta$-phase in PVDF. Further development of these pathways can lead to highly efficient TEGs capable of harvesting electrical energy from low-frequency mechanical impacts.

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