PDMS/PVA composite ferroelectret for improved energy harvesting performance

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Abstract. This paper address the PDMS ferroelectret discharge issue for improved long-term energy harvesting performance. The PDMS/PVA ferroelectret is fabricated using a 3D-printed plastic mould technology and a functional PVA composite layer is introduced. The PDMS/PVA composite ferroelectret achieved 80\% piezoelectric coefficient $d_{33}$ remaining, compared with 40\% without the proposed layer over 72 hours. Further, the retained percentage of output voltage is about 73\% over 72 hours.

1. Introduction
Ferroelectret are thin films of polymer foams which are can store electric charges in its internal voids, presenting strong piezoelectric-like properties after electric charging. The resulting macroscopic behavior of ferroelectret is very similar with the well-known piezoelectric material; but its charge generation mechanism is entirely different from the latter. For ferroelectret, the interior voids not only reduce the overall mass and stiffness, but also form great dipoles when the separated positive and negative charges are trapped on the top and bottom gas-polymer interfaces in the voids. When the ferroelectret is compressed by an external mechanical load, it can generate electric charges because the majority of dipole moment change take place in the voids [1]. Due to its high piezoelectric properties, ferroelectret are utilized as functional materials in electromechanical sensors and actuators also as electrically charged layers in electrostatic transducers [2, 3].

PDMS (Polydimethylsiloxane) is highly compliant and therefore suitable for integrating into wearable devices for harvesting kinetic energy from human motion. The PDMS gives conformal contact over large areas, even for substrates with uneven surfaces, and is easy to fabricate inexpensively. In addition, the PDMS is sufficiently elastic that it can be separated from the microstructure without destruction or distortion. However, the PDMS ferroelectret discharge significantly and only a small surface charge density which implies a very short lifespan of harvester and lower piezoelectric activity.

It is essential to solve the lower charge density and instability charge issue for PDMS ferroelectret. In this paper, a method of adding a functional PVA (Polyvinyl alcohol) composite film is presented to improve the lifespan of the harvester and enhance its piezoelectric effect due to PVA composite’s high dielectric permittivity and thermal stability.

2. Concept
As is shown in Figure 1, a PVA composite layer is introduced at the gas-polymer interfaces which is used as electrets to store charges. Our previous work has shown the relationship between the level of
piezoelectric activity and the geometry of the composite structures and its material properties [4]. Therefore, for a certain structure, the level of piezoelectric activity is proportional to the charge density of material. Compared with PDMS, the PVA composite has higher charge density and better thermal stability [5]. The combined PDMS/PVA ferroelectret harvester can further improve the energy harvesting performance and stability.

3. Experiment

3.1. Fabrication

The proposed PDMS/PVA composite ferroelectret is fabricated using a moulding process as illustrated in Figure 2. The plastic moulds were 3D-printed by a Connex350 TM 3D printing system (Stratasys, MN, USA). VerClear™ was selected as the mould material because it is transparent, which makes it easy to observe the entire fabrication process. Because the 3D printable material inhibits PDMS polymerization and the printed structure tends to warp to some extent when it is removed from the printer, the resulting 3D-printed mould is not immediately suitable for PDMS casting. Therefore the moulds are baked in oven at 80 °C for 24 hours. Next, the moulds were glued using a drop of degassed non-polymerized PDMS to a piece of clear glass. After this step, the glass-backed moulds were exposed to a silane vapour for 1 hour to be coated with a thin layer of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Sigma Aldrich, MO, USA). The final, baked moulds were flat and no longer inhibited the PDMS.

Once the plastic moulds are fabricated, liquid PDMS and curing agent (Sylgard 184 from Dow Corning, MI, USA) were mixed at a 10:1 weight ratio and the mixture degassed in a vacuum desiccator. The degassed PDMS was poured into the glass-backed mould which were again degassed and then baked at 80 °C for 1 hour. When the degassed PDMS was poured into the mould, the fluid level in the mould was monitored to ensure the degassed PDMS would not overflow. This step is used to control the thickness of the foam. Next, the PVA solution was prepared by dissolving 10g in 200 ml of distilled water in a glass beaker and stirred for 30 mins while being heated at 40 °C due to the higher solubility of PVA at this temperature. 2 g of ammonium salt was then dissolved in 100 ml of distilled water in another beaker and stirred for 30 mins at room temperature. The PVA solution and ammonium salt solution were then mixed together by electromagnetic stirring for 10 mins at 40 °C. The PVA composite solution is deposited by doctor blading to the flat PDMS layer. The composite films were baked in oven for 5 mins at 60 °C.

There are two possible methods to bond the two PDMS parts together: applying an adhesive or utilizing oxygen plasma machine. For the first method, degassed PDMS can be used as the. After detaching the polymerized PDMS from the moulds, the liquid degassed PDMS was painted on the part 1 with smooth surface and then the other PDMS layer was placed on to it, with its patterned surface in contact with the smooth surface (see figure 2). This bonding method was easy to implement but its was found to be difficult to control the amount of adhesive and overflow of the PDMS into the void would change the geometry of the whole cellular structure. In the second method, after detaching the polymerized PDMS from the moulds, an oxygen plasma treatment (Femto Asher, Diener, Germany, 30 S at 35-40W) was applied to both patterned surface of the PDMS part 2 and the smooth surface of PDMS part 1 (see figure 2) which are then bonded together. The bonded PDMS/PVA composite ferroelectret was baked in oven at 80 °C for 1 hour. A 10 N force was applied to the sample during the
bake to improve the bond quality, and also recover the original hydrophobic PDMS surface chemistry. The image of a fabricated PDMS/PVA composite ferroelectret is shown in Figure 3.

3.2. Testing
To investigate how the properties of the material are affected by the PVA composites, another pure PDMS ferroelectret was fabricated which is used for comparison. Both of these samples were polarized by a corona charging. A corona-tip voltage of -25 kV and a charging time of 2 mins were employed. The piezoelectric charge constant $d_{33}$ was measured using a PiezoMeter (PM300, Piezotest Ltd). To evaluate its energy harvesting performance, the output voltage of these sample were recorded using an oscilloscope. To quantify the applied forces on the test samples, an Instron electrodynamic instrument (ElectroPuls E1000, Instron Ltd) was used. The maximum dynamic force this equipment can produce is 1000 N and it can provide several types of compressive force including square, sinusoidal and triangular wave forces. The frequency of the compressive forces applied on the test samples was varied from 0 to 100 Hz. These parameters can be modified in the control software.

4. Results and discussion
Figure 4 shows a comparison of piezoelectric performance between PDMS ferroelectret and PDMS/PVA ferroelectret. The initial piezoelectricity of PDMS/PVA ferroelectret was about 110 pC/N which is 1.5 times greater than that of the PDMS ferroelectret. The PDMS/PVA ferroelectret retained
around 80% of its initial piezoelectric coefficients $d_{33}$ over 72h comparing with 40% for the pure PDMS material over 72h.

The output voltage of the PDMS ferroelectret and PDMS/PVA composite ferroelectret under compressive force takes the form of a voltage pulse as shown in figures 5 and 6. From figure 5, the maximal peak voltages measured 1 hour after corona charging for PDMS ferroelectret and PDMS/PVA composite ferroelectret were about 1 V and 1.5 V, respectively. In figure 6, the maximal peak voltage at 72 hours after corona charging for PDMS ferroelectret and PDMS/PVA composite ferroelectret were about 0.5V and 1.1 V, respectively. Thus the PDMS/PVA retains about 73% of its output voltage after 72 hours.

5. Conclusion
This paper presents PVA composite layer to address the PDMS ferro electr et discharge issue for improved energy harvesting performance. The PDMS/PVA ferroelectret achieves 80% piezoelectric coefficients retain rate over 72 hours, compared with 40% without the proposed layer over 72 hours. Device voltage retain rate is about 73% over 72 hours. These results prove that PVA composite is effective in extending the charge lifespan and enhancing the piezoelectric activity for PDMS ferroelectret. Future work will focus on further improving the charge density, stability for using another electret material.

Acknowledgements
This work was performed under the SPHERE IRC funded by the UK engineering and Physical Sciences Research Council (EPSRC), Grant EP/K031910/1.

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