Novel thick-foam ferroelectret with engineered voids for energy harvesting applications

Z Luo¹,², J Shi¹ and S P Beeby¹

¹Electronics and Computer Science, University of Southampton, Southampton, SO171BJ, UK
²School of Water, Energy and Environment, Cranfield University, Cranfield, MK430AL, UK

E-mail: z.luo@soton.ac.uk

Abstract. This work reports a novel thick-foam ferroelectret which is designed and engineered for energy harvesting applications. We fabricated this ferroelectret foam by mixing a chemical blowing agent with a polymer solution, then used heat treatment to activate the agent and create voids in the polymer foam. The dimensions of the foam, the density and size of voids can be well controlled in the fabrication process. Therefore, this ferroelectret can be engineered into optimized structure for energy harvesting applications.

1. Introduction
Ferroelectret is a porous polymer film that can store charges in its internal voids after charging. It is able to convert compressive force into electric pulses, which can be used for both sensing and energy harvesting. Despite being developed into sensing material for more than a decade, ferroelectret has attracted research interest in energy harvesting only in the recent years [1-3]. In the past, we demonstrated that multilayer ferroelectret is capable of powering the transmission of a low-power wireless chipset [1], and fabricated prototypes of ferroelectret-powered wearable devices [4]. The ferroelectret we investigated was commercial polypropylene (PP), which was fabricated by stretching the original polyolefin material and expanded into a foam. Hence, it is a thin polymer film with thickness less than 70 µm. This is favourable for sensor and actuator applications, but not for energy harvesting, since one layer of PP ferroelectret is not sufficient to power any electronic chipset [1]. The multilayer structure of ferroelectret can significantly increase the energy output [1, 4], but also hugely increases the cost and complexity in manufacturing.

Recently we have developed a novel thick-foam ferroelectret that is specifically designed and engineered for energy harvesting. This material was fabricated by mixing a chemical blowing agent with a polymer solution. The polymer solution can be moulded and cured into different shape and thickness. Thus the ferroelectret foam can be fabricated with thickness from several hundred microns to several millimetres. A schematic diagram of the foam’s fabrication comparing to the multilayer ferroelectret is shown in Figure 1. The blowing agent of the ferroelectret was activated at certain temperature and created cellular voids in the structure. The density of the voids was controlled by the concentration of the blowing agent, and the void size was controlled by the heating temperature and the heating time. Based on the model that we developed to predict the piezoelectricity of PDMS ferroelectret [5], and the electromechanical model to predict the energy output of ferroelectret [6], we were able to model and
engineer the void dimensions of the ferroelectret. This optimized structure was engineered by adjusting the processing parameters during fabrication. Compared to the conventional thin ferroelectrets which are mostly fabricated by stretching or foaming, this moulded ferroelectret can be fabricated in desired dimensions and its void size/density can be engineered. This is useful for optimizing the structure of the ferroelectret for energy harvesting applications, and potentially can be used to produce large-area ferroelectret.

2. Experimental

Low density Polyethylene (LDPE) was used as the polymer and Azodicarbonamide (ADZ) was used as the blowing agent. LDPE pellets were mixed with 0.2 wt% of ADZ powder. They were dissolved in xylene by heat treatment and stirring, and then left to dry for a week so the solution can solidify. In order to fabricate ferroelectrets with dimensions of 45 mm × 45 mm × 0.6 mm in this work, 120 g of solidified polymer was used to fabricate one layer of ferroelectret. The weighted portion was hot pressed in a mould at 130 °C with 3 tons of pressing weight for 1 min. This process can shape the solution into the desired dimensions and remove its bubbles. To activate the blowing agent, the hot pressed samples were heat treated in an oven at 230 °C for different durations of 1, 2, 3 and 4 mins, respectively. In this process, internal voids were created in the samples.

Electrodes were deposited on the top and bottom surfaces of the voided samples. The deposition was achieved using a Leybold E-beam Evaporator Lab 600. The deposited layers were 10 nm of Cr then 1 µm of Al. After the deposition, the samples were charged in a self-built needle-to-grid corona charging apparatus, with an electric field of 35 kV for 1 min. The charged samples were then ready to be tested as ferroelectret.

3. Results and discussion

The piezoelectric coefficient \( d_{33} \) of the ferroelectret was measured to be 200 pC/N using a Piezoetest PM300 \( d_{33} \) meter. Using a Wayne Kerr 4300 LCR meter to measure the electrical properties, the capacitance of the sample was 38 pF, resistance was 2.6 GΩ. Hence, the dielectric constant of the ferroelectret was calculated to be 1.27, indicating that a large number of voids are presented in the polymer.

During the heat activation, the ADZ blowing agents in the polymer decomposed and released gas. The expanded gas resulted in the void structure in the ferroelectret. A number of factors affects the density and size of the voids. Firstly, the concentration of the blowing agent obviously will determine the density of the void. Higher content of ADZ will create more voids in the sample. However, when the voids are too dense, the size of the void is more difficult to control since the neighboring voids tend
to merge into a bigger one. Hence, 0.2 wt% of ADZ content was used in this work. This is not the optimized content of ADZ for energy harvesting, but will create voids that can be easily observed and measured. Secondly, the activation temperature of ADZ is about 200 °C. Heating the samples above this temperature will accelerate the decomposition of ADZ. Thus at the same heating time, higher temperature will result in more gas and larger void size. In this work, heating temperature of 230°C was used for all the samples so the void size was altered by heating time only. Lastly, increasing the heating time will allow more gas to be released, thus larger void size. This is demonstrated in Figure 2, where the samples were heated for different durations. Voids with diameter of 90 µm was observed in the samples heated for 1 min, 140 µm for 2 mins, 310 µm for 3 mins, and 340 µm for 4 mins, respectively. It also shows that the growing rate of void size decreased as the heating time increased, because the size of the void tended to saturate when the ADZ fully decomposed.

![Figure 2](image_url)

**Figure 2.** Fabricated ferroelectret with different void sizes of (a) 90 µm; (b) 140 µm; (c) 310 µm; (d) 340 µm by heating for durations of 1, 2, 3 and 4 mins respectively.

From our previous study in modelling the piezoelectric output in ferroelectret, the optimized void size for high piezoelectricity is in the range of 50 to 100 µm [5]. Therefore, it is anticipated that the sample heat treated for 1 min will have stronger piezoelectric response comparing to the one heat treated for 2 mins. This is supported by the result from the experiment where the samples were under trapezoidal function of compressive forces, which has maximum amplitude of 800 N. The function of the force is shown in Figure 3 (a). The output pulses of the ferroelectret samples measured by oscilloscope are shown in Figure 3 (b) & (c). It shows that the maximum output of the sample with void size of 90 µm is 0.46 V and -1 V, the one with void size of 140 µm is 0.26 V and -0.88 V. The voltage output of the former is stronger than the latter, indicating a stronger piezoelectric response.
4. Conclusion and future work
This paper reports the design and fabrication of a novel ferroelectret material. It is fabricated by mixing a polymer solution with a chemical blowing agent ADZ, then shaped into desired dimensions by casting. The blowing agent is activated by heat treatment and create voids in the polymer. By controlling the parameters in the fabrication process, such as heating temperature and time, the size of the voids can be engineered. Hence, numerical simulation can be used to design an optimal void size, and achieving this size by adjusting the processing parameters. The next step forward will be to improve the energy output of the ferroelectret by varying the ADZ’s content and using different types of polymers as medium.

5. Reference
[1] Luo Z, Zhu D, Shi J, Beeby S, Zhang C, Proynov P and Stark B 2015 Energy harvesting study on single and multilayer ferroelectret foams under compressive force IEEE Trans. Dielectr. Electr. Insul. 22 1360-1368
[2] Zhang X, Wu L and Sessler G M 2015 Energy harvesting from vibration with cross-linked polypropylene piezoelectrets AIP Adv. 5 077185
[3] Anton S R, Farinholt K M and Erturk A 2014 An evaluation on low-level vibration energy harvesting using piezoelectret foam J. Intel. Mat. Syst. Struct. 25 1681-1692
[4] Luo Z, Zhu D and Beeby S 2015 Multilayer ferroelectret-based energy harvesting insole J. Phys. Conf. 660 012118
[5] Shi J, Zhu D, Cao Z and Beeby S 2015 Optimization of a PDMS structure for energy harvesting under compressive forces J. Phys. Conf. 660 012041
[6] Luo Z, Zhu D and Beeby S 2016 An electromechanical model of ferroelectret for energy harvesting Smart Mat. Struct. 25, 045010

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