Piezoelectrets with well-defined cavities produced from 3D-printed acrylonitrile butadiene styrene structures

Y.A.O. Assagra, R.A.P. Altafim✉, R.A.C. Altafim and J.P. Carmo

A novel piezoelectret with well-defined cavities produced by three-dimensional printing technology is reported. This prototyping tool allows many samples to be prepared in a single printing step and provides the possibility to design voided structures with control of the cavity geometric parameters such as height, diameter and shape. Acrylonitrile butadiene styrene piezoelectrets were fabricated by this method and measurements regarding their electrical response against time, temperature and pressure are presented. The samples show an average piezoelectric coefficient d_{33} of around 100 pC/N and 70% of this piezoelectricity remains after they were exposed to temperatures up to 85°C.

Introduction: Three-dimensional (3D) printing developed in the late 1980s for prototyping is promoting a revolution in different research areas. For instance, in medicine, the potential of 3D printing is being explored regarding the creation of biological organs and customised prostheses [1, 2] while in engineering, buildings and electronic devices are being produced through this technique [3, 4].

In the work reported in this Letter, 3D printing was employed in the creation of piezoelectrets, which are thin voided polymeric films, electrically charged which can exhibit piezoelectric behaviour [5]. The interest in these polymeric films relies on their inherent characteristics such as flexibility, low weight, reduced costs and electromechanical activity. This last characteristic is a consequence of electrical charges trapped on the internal voids' surfaces, which form macroscopic dipoles that are easily compressed [5]. These properties make piezoelectrets suitable for a variety of applications ranging from accelerometers to blood pressure sensors [6, 7].

In the past decade, different methods for producing piezoelectrets have been presented [5]; some of these concerned polymeric structures with well-defined cavities [8–10], which, according to [11], can lead to resonance frequency modulation if changes in the cavity geometrical parameters are performed. Controlled voided structures suitable for piezoelectrets have been produced with 3D printing technology [12] although it was used in the fabrication of plastic moulds employed on the preparation of polydimethylsiloxane structures. In this Letter, the 3D printing method is presented as an alternative method for creating piezoelectrets and its feasibility is demonstrated on samples made of acrylonitrile butadiene styrene (ABS) followed by measurements of temporal and thermal stability and pressure behaviour.

Piezoelectret: design and fabrication: Printed piezoelectrets were prepared using a 3D printer from Wanhao, model Duplicator 4× with a layer resolution of 0.1–0.5 mm. The printer is based on a method called fused deposition modelling, where thermoplastic filaments are melted and extruded layer-by-layer into a pre-designed CAD object. Different polymers can be employed in this process, for instance, ABS, poly (vinyl alcohol) or polylactic acid. For this work, ABS was chosen due to its electrical properties [13, 14]. The main advantages of the 3D printing process relate to the full control of cavity shapes and their geometrical parameters, such as height and thickness, and the possibility to prepare several samples in a single printing step. Thus, several samples were printed at the same time, however, each sensor consisted of two separated printed films with 40×40 mm^2. One of the films was designed with 100 µm thickness and both surfaces flat; the other was designed with a total thickness of 200 µm being one flat surface and another containing a circular 3D structure of 100 µm height, as shown in Fig. 1*a*. The circular structures formed the necessary air cavities after the films were stacked and sealed at the edges with a plastic sealer. Later, metal electrodes adhesives were stuck on both samples' surfaces and a DC voltage of 4.5 kV was applied. Images of the circular voided structure and the finished piezoelectret sensor are presented in Fig. 1*b*.

Electromechanical measurement: The electromechanical behaviour of piezoelectrets can be represented as the piezoelectric coefficient d_{33} given by the following equation [10]:

$$d_{33} = \frac{Q}{F} \tag{1}$$

where Q is the electric charge and F is the applied force.

To determine the electrical response of the printed piezoelectrets, a pressure device was built based on the pneumatic loading method (PLM) previously described in [15]. The measuring system consists in applying a direct pneumatic pressure to the samples' electrodes causing a mechanical deformation that disturbs the electrical charges, equilibrium providing an electrical signal. In this system, the sensor was placed over a grounded contact ring with an open diameter of 1.5 mm, to leave one side of the sample exposed. After placing the sample, a pneumatic piston containing a top electrode was activated to compress the sample with a load ensuring electrical contact. The exposed area was connected to a pneumatic valve, which releases pressurised air over the sample. A pressure gauge from SMC, model ISE30, was employed to measure the applied pressure, which was adjusted to 20 kPa. The sensor's electrical response was recorded with a Keithley electrometer, model 6517B, in the charge mode.

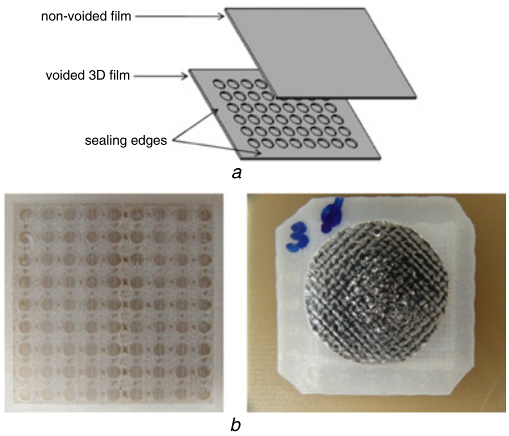

Fig. 1 *Concept of piezoelectret 3D printer sensor before assembling films (Fig. 1a), and top view of 3D printed voided structure and piezoelectret sample with electrode (Fig. 1b)*

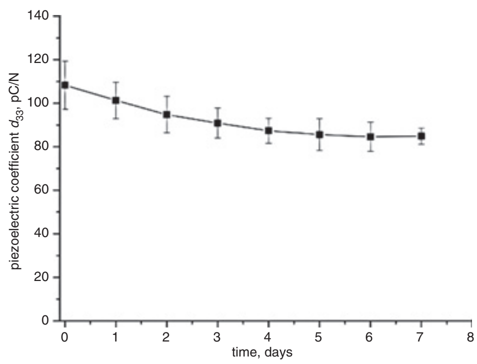

Fig. 2 *Piezoelectric coefficient d_{33} plotted against time, indicating decay of 18% of its initial value*

Results and discussion: One of the major concerns that affects piezoelectrets is the electrical charge stability, which is responsible for the piezoelectricity observed in these films. Therefore, it is natural that researchers seek more electrical stable polymers in order to enhance piezoelectrets' performance. Since most electric stable polymers are fluoropolymers, which are not easily processed into a 3D printer, the initial concern was to verify the temporal stability of ABS piezoelectrets. From previous work [13], it became known that negative charges are relatively stable in such polymeric material, however the electrical behaviour of piezoelectrets depends on both positive and negative charges, thus measurement of the piezoelectric coefficient d_{33} was performed in relation to time and the result is presented in Fig. 2. As can be observed in Fig. 2, the piezoelectric coefficient d_{33} presented a small decay in the first five days, representing a loss of 18% on their initial value, although after this period the samples reached stabilisation.

Another aspect related to piezoelectrets research regards their thermal stability, which is motivated by the fact that elevated temperatures promote electrical charge detrapping, reducing their piezoelectricity [10]. Therefore, in order to verify ABS piezoelectrets' thermal stability, a measuring technique named *short-term thermal stability* was applied to the samples. The method consists in initially measuring the d_{33} coefficient at room temperature (25°C) and then subsequently heating them for one hour at specific temperatures. Here, an oven was set to the following temperatures: 35, 50, 70 and 85°C. It was observed that the ABS piezoelectrets started to deform at temperatures above 85°C. After exposing the samples to the selected temperature they were cooled to ambient conditions and the d_{33} was again determined. The results are presented in Fig. 3.

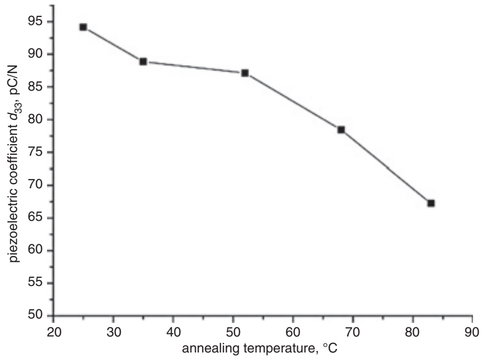

Fig. 3 *Piezoelectric coefficient d_{33} after exposing piezoelectrets for one hour at specific temperatures*

Fig. 3 shows a piezoelectric coefficient d_{33} decay of ~7% after the samples had been exposed to temperatures up to 50°C. Above this temperature, the losses become more pronounced, but 70% of the initial piezoelectric coefficient was still present on the samples after they were exposed at 85°C. This thermal stability is higher than those observed on chemically treated polyethylene (PE) piezoelectrets [16] and is comparable to those obtained on PE-naphthalate (PEN) [17] although it is below the thermal stability of fluoropolymers, which are stable at temperatures up to 100°C [8].

As well as temporal and thermal stability, the main characteristic of piezoelectrets is their electromechanical behaviour and in order to verify the influence of different pressures on the electrical response of the ABS samples, the pressure in the PLM setup was varied from 20 to 55 kPa while d_{33} was determined. The results shown in Fig. 4 indicate that at lower pressures, i.e. below 25 kPa, the 3D printed piezoelectrets present a piezoelectric effect comparable to those obtained with on cellular PEN films [17] and it shows a decay behaviour with the pressure increase.

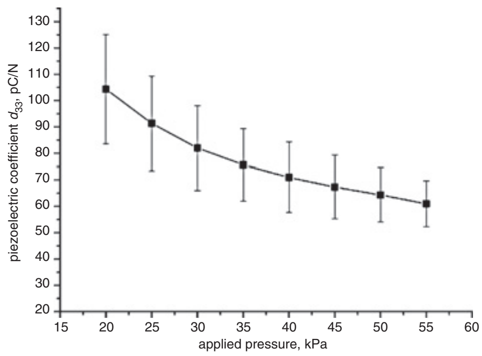

Fig. 4 *Influence of pressure on piezoelectric coefficient d_{33} of 3D printed ABS piezoelectrets*

Conclusion: 3D printing technology was explored to create new piezoelectrets made of ABS. The process presents some important advantages on piezoelectret prototyping, which are the preparation of many samples in a single printing step and the possibility to control all cavities' geometrical parameters. The ABS piezoelectrets produced by this technique showed a piezoelectric coefficient d_{33} of around 100 pC/N, which was stable at room temperature during the measuring period. The samples presented a thermal stability comparable to those exhibited by PEN piezoelectrets. During a pressure behaviour investigation, the ABS piezoelectrets were able to sense pneumatic pressures of 20–55 kPa, showing an exponential decay with the pressure increase.

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One or more of the Figures in this Letter are available in colour online.

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