Piezoelectric cellular micro-structured PDMS material for micro-sensors and energy harvesting

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Abstract. This paper reports a novel low-cost fabrication process of a charged cellular micro-structured polydimethylsiloxane (PDMS) material referred as piezo-electret or ferro-electret for micro-sensors applications. The dielectric spectra reached on these structures exhibit a high piezoelectric longitudinal coefficient $d_{33}$ of 350pC/N. A mechanical characterization method proves the reliability of this material for low-frequencies applications around 100Hz.

1. Introduction

Piezoelectric materials are widely used in the micro-sensors and the actuators field. Depending on the desired applications, specific properties like piezoelectric parameters, the patterning process, the mechanical stiffness and the thermal stability may be taken into consideration and properly adjusted. During the last fifteen years, the implementation of the materials referred as piezo-electrets or ferro-electrets have opened new opportunities in the sensors and actuators design due to their mechanical flexibility and piezoelectric properties. Ferro-electrets or piezo-electrets are composite materials, which are presented in the matrix form containing internal voids organized in a regular or random way. These structures become piezo-electrically functional once opposite charge carriers are implanted in the inner voids’ surfaces. These charges are responding to quasi-permanent macro-dipoles, the piezoelectric activity arises from the changes of these internal dipole moments resulting from the mechanical or electrical stresses in these materials. The piezoelectric materials have been already implemented in many applications. In fact, they were used in artificial muscles, microphones, loudspeakers, in shoes for converting mechanical energy into electrical energy, for flexible array position detectors (touchpads) and stretchable large array pressure sensors. In order to control the piezoelectric properties of this structures type, a fabrication process for controlling the shape, the size and the spatial distribution of the voids in the polymer matrix is required. These structures usually exhibit a high piezoelectricity in the thickness direction characterized by a large piezoelectric coefficient $d_{33}$. This constitutes an advantage for applications requiring electro-mechanical transduction in the thickness direction. The thickness piezoelectric coefficient $d_{33}$ can be easily determined through their direct or converse piezoelectric response. In this paper, we propose a novel low-cost fabrication process of the charged cellular micro-structured polydimethylsiloxane (PDMS) material for ferro-electret micro-sensors and energy harvesting applications. We proposed the dielectric spectroscopy as a powerful tool to test the performance of the PDMS ferro-electret and a mechanical method exhibiting the reliability of such structures for low-frequencies applications.
2. Sample preparation
The polydimethylsiloxane (PDMS) used in this work was prepared using the Sylgard 184 Silicone Elastomer Kit from Dow Corning. The kit is composed of two elements: the pre-polymer (dimethyl-vinyl terminated silicone base polymer) and the curing agent. These elements were mixed at 1:10 weight ratio recommended by the supplier and also used by other authors [1]. The obtained mixed uncured PDMS was degassed in a vacuum desiccator. To develop the cellular micro-structured PDMS material, we proposed a low-cost method that enables us to control the size and the shape of the micro-cavities introduced in the PDMS polymer. The process was carried out in three steps. Firstly, the molds for the micro-structured layers were made using a photosensitive dry film (Riston® MM540, Dupont) bonded to the substrate and a photo-mask, the package was inserted into the UV curing machine (Krub, Kloé) to be exposed to 50% of the maximum power during 20s for the photolithography. Then, the photosensitive film was developed using a 1% anhydrous Sodium Carbonate solution ($\text{Na}_2\text{CO}_3$). The obtained molds are made up of cylindrical pads with a height of 40µm, a diameter of 100µm and a pitch of 150µm (Figure 1). The micro-structured 40µm thick layers were obtained by spin-coating the PDMS on the molds that had already been made. Bulk 55µm thick layers were also obtained by the same technique. The thickness of the PDMS layers was checked with a mechanical sensor (Mitutoyo). The micro-structured PDMS material is presented in the form of a sandwich of three layers, two bulk layers of 55µm thickness separated by a micro-structured layer of 40µm thickness (Figure 2). The three layers were bonded together using oxygen plasma treatment for 2s. Our structures were considerably minimized compared to those implemented by previous work [2].

![Figure 1. SEM top view of the micro-structured layer with bottom bulk layer.](image1)

![Figure 2. Schematic illustration of the micro-structured PDMS material with top and bottom gold electrodes.](image2)

3. Electrical charging
In this study, we used the contact charging, which is the most promising technique for the electrical charging of such structures that can be performed with simple equipment. This technique consists of applying a quasi-static voltage directly across the gold electrodes that have been deposited in advance onto the sample surfaces. The applied electric field that is estimated by the Paschen’s law, triggers the electric breakdown into the micro-cavities to generate the macro-dipoles. We chose to charge our structures by applying a quasi-static triangular voltage across the sample electrodes with amplitudes between 1kV and 4kV with a frequency of 0.5Hz for 15min. The electrical charging equipment is composed of a function generator [Keithley, 3390, 50MHz] coupled with a High Voltage amplifier [Spellman, SL60] in order to provide the needed amplitudes. The amplifier has a breakdown detector to protect the equipment and the samples. The electrical charging cell is provided with electrodes of smaller areas than these of the samples. The cell is installed in a thermalized chamber.

4. Results and discussion
4.1. Dielectric-resonance spectra
The method of dielectric-resonance spectra relies on the converse piezoelectricity of the sample. In fact, the structures deform upon an application of a voltage and vibrate periodically if they are subjected to an ac-voltage. If the ac-frequency coincides with a structure mechanical vibration mode, a resonance will be detected. Dielectric properties of the poled cellular micro-structured PDMS ferro-
electret material were reached with the dielectric analyzer [Novocontrol, BDS 20]. Samples were placed in a vacuum chamber to avoid parasitic effects and interferences during the measurements. The temperature was controlled by the temperature programmer [Linkam, TMS94]. All measurements were made under inert gas (Nitrogen) to avoid the oxidation phenomenon at high temperatures. Samples were subjected to an alternative voltage of $1V_{rms}$ in the frequency range $100Hz$ to $1MHz$ and in the temperature range from $-25^\circ C$ to $85^\circ C$ by a step of $10^\circ C$. The electroded samples were brought into contact with two measuring points that could vibrate freely with the applied sinusoidal voltage, with only minimal effects from spring-loaded electrode contacts. Figures 3 and 4 represent the frequency-temperature map of the dielectric loss $C''$ of the non-charged and charged at $25^\circ C$ cellular micro-structured PDMS material, respectively.

**Figure 3.** Frequency-temperature map of the dielectric loss of the non-charged micro-structured PDMS material.

**Figure 4.** Frequency-temperature map of the dielectric loss of the charged micro-structured PDMS material at $25^\circ C$.

We can observe the resonant phenomena that appear in Figure 4 compared to Figure 3. The dielectric resonance loss $C''$ spectrum of the piezoelectric micro-structured material near the thickness-extension (TE) mode anti-resonance frequency can be fitted by a least square fit method through the imaginary part of Equation 1 [3, 4].

$$\begin{align*}
C(f) &= \frac{\varepsilon_0 \varepsilon_r A}{h} \frac{1}{1-k_{33}^2} \frac{\tan(\pi f/2 f_p)}{(\pi f/2 f_p)} \cdot iC_{loss} \\
C_{loss} &= \frac{\varepsilon_0 \varepsilon_r A}{h} \frac{1}{1-k_{33}^2} \frac{\tan(\pi f/2 f_p)}{(\pi f/2 f_p)}
\end{align*}$$

Where $\varepsilon_0$ is the permittivity of the free space and $\varepsilon_r$ is the relative permittivity of the sample, $A$ and $h$ are the electroded sample area and the thickness, respectively. $k_{33}$ is the complex coupling factor and $f_p$ is the complex anti-resonance frequency of the TE mode. $C_{loss}$ is related to the loss that can occur in the material other than those related to the resonance phenomena. $f_p$ is related to the complex elastic stiffness $c_{33}$ and the sample mass density $\rho$ through Equation 2.

$$f_p = \frac{1}{2h} \sqrt{\frac{c_{33}}{\rho}}$$

The coupling factor $k_{33}$, is given by Equation 3.

$$k_{33}^2 = \frac{d_{33}^2 c_{33}}{\varepsilon_0 \varepsilon_r}$$
$f_p$, $k_{33}$, and $C_{loss}$ are determined via the fit for each temperature; then, $c_{33}$ and $d_{33}$ were calculated via Equations 2 and 3, respectively. The temperature dependence of these quantities is shown in Figures 5 and 6.

![Figure 5. Temperature dependence of the real and imaginary stiffness $c'_{33}$ and $c''_{33}$.](image1)

![Figure 6. Temperature dependence of the coupling factor $k'_{33}$ and the piezoelectric coefficient $d_{33}$.](image2)

The micro-structured PDMS material shows a low constant elastic stiffness in the temperature range between -25°C and 85°C (Figure 5). However, the low real part of the elastic stiffness $c'_{33}$ is accompanied by an important imaginary part $c''_{33}$, even exceeding the real part. The electromechanical coupling factor $k'_{33}$ represents a maximum value of 0.055, this value matches the maximum value of the piezoelectric coefficient $d_{33}$ of 350pC/N at 25°C. This temperature corresponds to the temperature of the electrical charging process. Moreover, a high compliance modulus of the PDMS, increased by the structure morphology, boosts the piezoelectric coefficient $d_{33}$ and thus the piezoelectric effect of the material. When samples are heated and attain 60°C, $d_{33}$ decreases considerably compared to its maximum value due to the thermally stimulated loss of internally implanted charge carriers. However, the cellular micro-structured material is still piezo-electrically operating over a wide temperature range from -25°C to 85°C.

4.2. Electromechanical piezo-electret sample testing

The experimental setup used for the electromechanical testing of our structures is similar to that used in work published by Hillenbard and Sessler [5], and Kressmann [6]. The micro-structured PDMS piezo-electret material connected with a wideband charge amplifier (B&K 2634) and loaded with an additional mass of $m=0.1kg$ on its top surface is actuated with the shaker (Data Physics -V20) in a frequency range from 10Hz to 200Hz. The shaker acceleration is set to $a=0.4m.s^{-2}$. When the piezo-electret sample is under excitation, two forces act on the sample: the static force, $f_s$, from gravitational acceleration $g$ and the dynamic force, $f_d$, related to the acceleration $a$ imposed by the shaker to the vibrating mass given by Equation 4.

$$f_s = mg; f_d = ma$$  \hspace{1cm} (4)

The dynamic force is responsible for the generation of charge carriers on the electrode surface and retrieves the response by the charge amplifier (Figure 7).
Figure 7 shows a force sensitivity of 30pC/N at the vicinity of 110Hz, which can head towards a use of such micro-structured ferro-electret PDMS material as a micro-sensor in a low-frequency range. The resonance-determined $d_{33}$ is much larger than that obtained from the electromechanical testing. This can be explained by the different measurement conditions used in these two techniques. In fact, for the electromechanical testing method, in addition to the dynamic force used to calculate $d_{33}$, the sample is loaded with a static force in order to be fixed. Therefore, as the cellular material is compressed, its elastic modulus increases, which decreases the $d_{33}$. This fact is valid especially for this type of samples presenting a very low elastic moduli. Contrarily, during the resonance determination, the sample is free-standing, and can vibrate freely without any extra load.

5. Conclusion and future work

In this work, a novel low-cost method for implementation of cellular micro-structured ferro-electret PDMS material was proposed. This process allows us to control the shape and the size of the cellular structures. The piezoelectric properties of such structures, investigated using the dielectric resonance spectroscopy, result in high piezoelectric coefficient $d_{33}=350pC/N$. An additional electromechanical testing shows a force sensitivity of 30pC/N at a frequency of 110Hz to confirm the reliability of such structures as micro-sensors for low-frequency applications. In the future, we will improve the piezoelectric response of these miniaturized structures for energy harvesting.

6. References

[1] Johnston I D, Mccluskey D K, Tan C K L and Tracey M C 2014 J. Micromechanics Microengineering 24 035017
[2] Shi J, Zhu D and Beeby S P 2014 J. Phys. Conf. Ser. 557 012104
[3] Mellinger A, Wegener M, Wirges W and Gerhard-Multhaupt R 2001 Appl. Phys. Lett. 79 1852–4
[4] Fang P, Holländer L, Wirges W and Gerhard R 2012 Meas. Sci. Technol. 23 035604
[5] Hillenbrand J and Sessler G M 2004 IEEE Trans. Dielectr. Electr. Insul. 11 72–9
[6] Kressmann R 2001 J. Appl. Phys. 90 3489–96