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Piezoelectrets: a brief introduction

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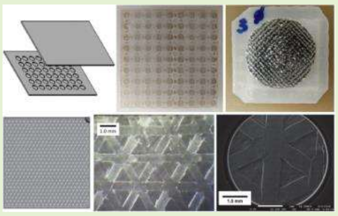
***Abstract*—Piezolectrets are thin polymeric structures with internal cavities that are electric charged. The bipolar-trapped charges form macro-dipoles that can be easily deformed, thus exhibiting high piezoelectric coefficients, i.e. in the order of hundreds of pC/N. exceeding the performance of the most traditional piezoelectric polymers. Piezoelectrets can be manufactured by different polymer processing, some of the techniques allows the inner cavities to be geometrically controlled providing some degree of freedom in the piezoelectric behavior. This report provides a description of most relevant methods, starting with a brief piezoelectret origin and reaching the most recently developments in piezoelectret production i.e. additive manufacturing (3D printing). Materials that are regularly employed in piezoelectret fabrication and methods for improving their characteristics are also presented.**



***Index Terms*— electret, piezoelectret, piezoelectret sensor, manufacturing processes, 3D printing**

I. INTRODUCTION

THE decade of 1950s is marked on the history of piezoelectricity as the period of time in which the first researches with polar polymers of biological origin, called biopolymers, appeared. The effect, first observed in wood pieces by Bazhenov was further investigated by Yasuda and Fukada, in materials such as bones, collagen and cellulose [1-2]. These works promoted a fundamental base for Kawai, in 1969 demonstrate the piezoelectric effect on films of polyvinylidene fluoride, (PVDF $[-(C_2H_2F_2)_n-]$). Discovery that not only allowed the industrialization of products but also brought some important advantages such as large scale production (when compared to ceramics), more flexible, less density and acoustic impedance similar to that of air [2,3].

Parallel to the discovery of piezoelectricity in polymers, another research that gain attention in that time was those related to electrets transducers [4], where layers of electrets with different densities were being proposed as a new form of transducer [5]. From a macroscopic point of view, the transducing electret effect is very much similar to those observed on piezoelectric materials. This similarity led Wada and Hayakawa, in 1976, to demonstrated that piezoelectricity could also be observed on overlapping layers of electrets formed from trapped electrical charges.

Regarding, these phenomena, researchers began to combine soft and hard electret layers to improve transducer applications [3,5-7].In 1987, it was proposed an alternative transducing material, named Electromechanical Film (EMFi), made from foamed from polypropylene (PP) films electrically charged [Patent]. The films contained cell cavities (or microbubbles) inside, and thin, smooth and homogeneous outer layers of the same material, by a process involving extrusion and aeration. After charging, the lower and upper surfaces of the cavities showed opposite polarity charges, thus having electrical micro dipoles. A piezoelectric sensitivity above 600 pC/N was found [8]. The high piezoelectric coefficient (PC) exhibited by the polymeric foams stimulated research with polymeric transducers. Subsequently, studies have shown that the property of trapping the characteristic electrical charges of electrets and the low mechanical stiffness of the porous films resulted in high electromechanical effect. As a result, the electrically charged polymeric foams, or cellular polymers were designated electromechanical films, ferroelectret or piezoelectret films, in reference to the concepts involved [4].

As the thermal stability of piezoelectric transducers is a limiting factor for certain practical applications, knowledge of this characteristic is of paramount importance, especially in situations where sudden changes in temperature occur. In these cases, errors in measurements or even absence of signal can be observed [4,5]. Piezoelectrets based on porous polypropylene (PP) films have the need for further research and development, since they have low thermal stability, which is around 60ºC [11], thus limiting its applications. In this context, new polymeric structures with more thermally stable materials have been proposed, with emphasis on the arrangement formed by the combination of porous and non-porous films, simulating the behavior of cellular polymers.

Among the new polymers used in the production of piezoelectrets, polyethylene naphthalate (PEN) stands out, with an application temperature of up to 80ºC. Fluoropolymer films, such as polytetrafluoroethylene (PTFE) and fluorinated propylene ethylene (FEP), cycloolefin and their copolymers,

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Teflon® AF have a thermal stability above 80ºC [3,4]. Even with piezoelectrets, showing advantages related to the application temperature, techniques to increase the thermal stability of these materials are being studied. Although several studies with more thermally stable polymers have emerged, most of these polymers are not found in the form of porous films on the market. Thus, many researchers have used convenient extrusion techniques and even the development of different methods to obtain these films [11-15].

Some techniques developed by researchers to obtain porous films, are considered classic, with emphasis on: extrusion followed by bidirectional stretching [15]; submitting films to pressure loading with subsequent heat treatment [20] chemical treatments with nitrogen and carbon dioxide injection [11,17]; insertion of mineral particles or hollow microspheres of glass into the film [13,18,19]. In addition to these techniques, there is also: film treatment with supercritical carbon dioxide fluid [20]; insertion of plastic microspheres containing gases such as isopropane or isobutane [21]; combination of three layers of films (non-porous, porous and non-porous) [17,22] and multilayer structure (four or more) of porous and non-porous films [23].

With the spread of 3D prototyping, a new method for the development of piezoelectrets and ferroelectrets by 3D printing has emerged. Thus, with this new approach to the design and construction of piezoelectrets via 3D prototyping, two innovative proposals arise.

The first in 2015, Assagra et al., proposed a technique for producing piezoelectrets by 3D printing using acrylonitrile butadiene styrene (ABS). It was possible to build a two-layer film structure, with regular sized cavities and precise geometry control reaching PC's around 100 pC/N and a 30% drop in PC [24] after being exposed to temperatures up to 85 ºC. The second approach, in 2020, Assagra et al. proposed a more elaborate technique. After several tests, it was possible to improve the printing parameters such as speed, temperature of the printing table and filament, percentage of filling and geometry, by using polypropylene (PP) filament was used. In addition, it showed PC around 200 pC/N, similar to the PC values obtained in ferroelectrets produced by traditional techniques and a 17% drop in PC [25] after being exposed to temperatures up to 80 ºC.

II. PIEZOELECTRETS

Sessler asserts that electrets can be defined as dielectric substances almost permanent electrified [26]. Another definition, proposed by the German physicist Bernhard Gross and the French physicist Line Ferreira-Denard, defines electrets as materials which, after subjected to an electric field remains electrically polarized [27].

A. The Electret

It can be said that the history of electrets began in 1732, when British scientist and astronomer Stephen Gray observed that materials such as waxes and resins were capable of permanently attract light bodies the same way of those reported by Plato. After these materials were melted and cooled, their attraction behavior could be observed [28].

The research on electrets began in 1839 with the publication of the British scientist Michael Faraday's studies defining the materials in which electrical forces acted as dielectrics. In these studies, it was showed that electric particles do not move freely when they are under the influence of an external electric field, thus remaining trapped in the material's structure when the electric field is removed [29]. Due to its resemblance to magnetic materials (magnets), The English scientist Oliver Heaviside, in 1892 attributed the term "electret" to dielectric materials capable of exhibiting permanent polarization [29].

In 1919, Mototaro Eguchi produced the first electret using the thermal method by melting equal parts of carnauba, beeswax and resin at a temperature of approximately 130 ºC, forming a disk with 20 cm of diameter and 1 cm thick. Then, he let the mixture solidify while being subjected to a strong electric field of 1.5 MV/m. After producing this first electret, which has remained charged after 45 years, Eguchi realized that the composite exhibited two distinct types of polarization. An initial polarization with electrical charges opposite to that of the contact electrode and formed by free ions and molecular dipoles present in the composite, designated as heterocharges; and another with electrical charges of the same signal as those present on the electrodes, homocharges [2,30,31].

However, even with Eguchi's observation about the difference between the origins of electric charges, only in 1944 Bernhard Gross, based on the ideas presented by Mikola [32], Adams [33] and Gemant [34], demonstrated the effective difference between the distribution of space charges and polarization by electrical dipoles, defining the terms homocharges and heterocharges [35]. Gross published his hypotheses regarding the origin of permanent polarization in electrets as two successive processes. In the first process, the orientation of the molecular dipoles and space charges (responsible for the origin of the heterocharges) occurs. After the electric field ceases, the second process begins, which is the injection of electrical charges from the electrodes (responsible for the origin of the homocharges), as proposed by Faraday in 1837 [3,5,29]. Fig. 1 shows the schematic of the two processes, the orientation injection of molecular dipoles and of spatial charges, and the injection of charges from the electrets.

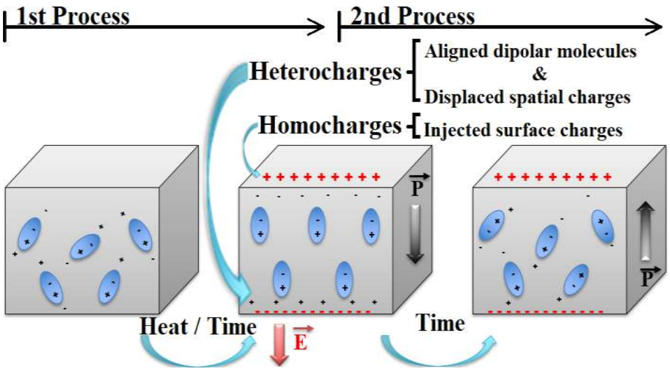

Fig. 1. Schematic representation of the electrical charge configuration of the electrets produced by Eguchi, on left before polarization; in middle after the electric field ceases; and on right after time has elapsed.

Gross's theory, which significantly contributed on the understandi of electrets, is divided in two processes. In the first one, the application of the electric field causes the alignment of dipolar molecules and the displacement of spatial charges of the dielectric, trapping charges inside the material. Furthermore, there is the injection of electrical charges on the surface of the dielectric of the same signal as the forming and adjacent electrets. Immediately upon ceasing the electric field, the second process begins, with a greater electric field originated by the dipolar molecules and the spatial charges displaced in relation to those of the injected charges. The orientation and the sense of the resulting polarization $\vec{P}$ are both equal to those of the applied electric field $\vec{E}$, as represented in fig. 1 (middle). However, there is a gradual decrease in magnitude of $\vec{P}$ caused by the relaxation of molecular dipoles and the movement of spatial charges. After $\vec{P}$ becomes zero, it gradually increases in magnitude in the opposite direction of $\vec{E}$. This occurs when the contributions of the electric fields of the spatial charges begin to overlap with the fields of the molecular dipoles and spatial charges, as shown in fig. 1 on (right). Thus, the polarization reversal of the electret occurs due to the temporary nature of the heterocharges (molecular dipoles and spatial charges), as well as the predominant contribution of the homocharges (injected charges).

After the confirmation of Gross' theory, electrets were a great focus of studies with the use of new polarization techniques. Among these techniques, the photopolarization is a highlight. This method consists of submitting the sample to the action of a light and permanent electric field. Through this method of polarization, it were originated the Nadjakoff's photoelectrets, resulting in applications such as the electrophotographic [3,29].

The electret formation process can occur in several ways, depending on the type of material used. In semi-crystalline and polar polymers such as PVDF, polarization occurs through the alignment of the molecular dipoles by applying an external electric field and high temperature conditions. In non-polar polymers, such as fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE), by applying an intense electric field, electric charges remain trapped, either on the surface of the polymer or in its volume [36]. The volume traps can be caused by structural anomalies, such as impurities, defects of the monomer units, irregularities of the chains and imperfections of the crystallites. Surface traps, can be caused by chemical impurities, specific surface defects caused by oxidation, chain breakage and adsorbed molecules [36].

The trapping of charges in the polymers can be interpreted according to a modified energy band model, fig. 2 (left), in which the traps are localized states belonging to certain molecules or molecular groups. In amorphous, polycrystalline or partially crystalline materials, local energy levels are affected by their environment and differ in each molecular region of the material. Thus, there is a randomness associated to the depth of the traps along the material [37]. Non-localized states, known as extended states, are positioned energetically close to the lower part of the conduction band and the upper part of the valence band. A possible density distribution of these states is shown in fig. 2 (right) [37].

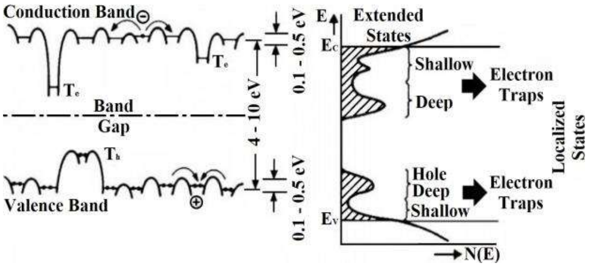

Fig. 2. Energy diagram (left) for a polymer, where Te are the electron traps and Tl gap traps. ; density of energy states N(E) for a polymer (right), in which the located states (traps) are shaded; Ec and Ev are the mobility edges of the conduction band and the valence band.

It can be seen from Fig. 2 the separation of the traps from the not allocated states by the so-called mobility edge, in which the mobility of the carriers decreases several orders of magnitude. Carriers in these energy states move through mechanical quantum leaps. Although the extended state plays a role in charge carriers transportation [37], the charge trapping in the extended state of electrets is minimal. That way, the application of the external electric field can be performed by different methods.

B. Piezoelectrets Charge

This method, due to the simplicity of implementation and its efficiency, is considered the traditional method for piezoelectrets polarization. Fig. 3 shows the configuration of the system used for this type of charging.

a. Polarization by direct contact

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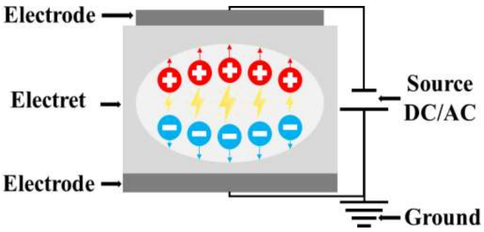

Fig. 3. Direct contact charging.

By applying the electric field, electric charges migrate from the electrodes to the contact surface of the dielectric, becoming trapped in it, causing the material to be polarized. As an attempt to balance the applied electric field, the free electric charges move in opposite directions to their polarization, remaining at the interface or in the volume of the dielectric, influencing the final polarization of the material [11].

b. Corona discharge polarization

In this method, a flat and a point-shaped electrode configuration is commonly used, as shown in Fig. 4 (left). The point-shaped electrode promotes the formation of the corona discharge when a few kV/cm field intensity is reached. The applied electric field generates an ionized region near the upper electrode (tip), accumulating positive or negative charges according to the applied voltage polarity. These ions are accelerated in the direction of the lower (plane) electrode by the action of the applied electric field and, when they reach the dielectric, are trapped in the surface or volumetric traps of the material [39].

Despite its simplicity, there are some disadvantages charging an dielectric by the corona discharge process. Some of them are: lack of measuring control of the amount of charges deposited on the dielectric surface, as well as the non-uniform charge distribution as a result of this technique. However, it can be addressed by inserting a metallic grid connected to another DC source between the point electrode and the dielectric material [39]. Fig. 4 (right) represents the optimized configuration of corona charging, also known as the triode-corona system.

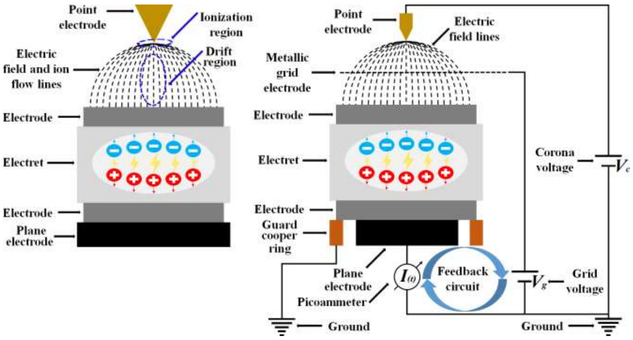

Fig. 4. Corona discharge (left) produced with plane-point electrodes, and triode-corona system (right).

In the triode-corona configuration, the electrical potential applied to the grid (V_g) limits the surface potential of the dielectric while the charging current ($I_{(t)}$) is monitored [40]. Besides defining the electrical potential on the surface of the dielectric, this configuration results in a more homogeneous charge distribution.

C. Material

Polymeric foams have being used mainly in the production of plastic packaging and thermal, electrical or acoustic insulation [41]. Compared to non-porous polymers, foams have a lower density and greater ease of compression, which makes them excellent materials for applications in electromechanical transducers, if they can trap charges as electrets [42]. In this context, porous polypropylene (PP) films were produced by a co-extrusion process in order to transform the energy of an electric and magnetic field into mechanical energy, and conversely, mechanical energy into electrical energy [9]. After the co-extrusion process, the porous films went through a bidirectional stretch with the purpose of modifying the circular geometry of the cavities, significantly reducing the foam elasticity modulus.

During the stretching process, the small internal fibers of the material are destroyed, contributing to the reduction of elastic stiffness [15]. Besides the elastic improvements, the produced cavities contributed to the formation of large dipoles when the polymer was subjected to an intense electric field. The combination of the elastic properties and the imprisonment of electric charges revealed a piezoelectric effect far superior to those found in the polymers known until then. Due to the similarity with the electrets and the high PC exhibited, these cellular polymeric structures received the name of piezoelectrets or ferroelectrets [18, 42]. Therefore, piezoelectrets, as well as electrets, need to be polarized in order to have electromechanical effects. However, the polarization process of piezoelectrets differs from the traditional electrets process previously described, since their polarization is based on the dielectric rupture of the gas present inside the porous film cavities. During the breakdown, electrical charges of opposite polarities are produced and trapped in surface traps of the internal cavities, forming electrical dipoles as shown in Fig. 5.

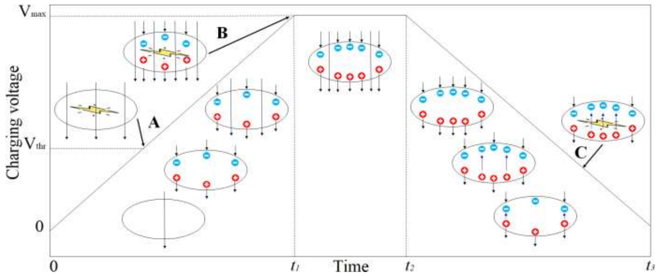

Fig. 5. Schematic view of the polarization process in a single cavity.

It can be seen from Fig. 5 that the polarization of the cavities occurs only when the applied electric field reaches a minimum value (point A). At this moment, an internal electrical discharge (Paschen breakdown) is triggered in the cavity and charges with opposite polarities are separated and trapped in the upper and lower surfaces of the cavity. The trapped charges, then, produce an internal electric field in the opposite direction to the applied field and, consequently, extinguish the discharge. As the applied voltage increases, a second discharge can occur and the density of trapped charges increases considerably, as seen at point B of Fig. 6. When the applied voltage is reduced, the electric field generated by the trapped charges can exceed the applied electric field and produce a back discharge (point C), canceling a significant amount of the effective charges [38].

The high PC manifested by the piezoelectrets is explained by the fact that, when subjected to an external mechanical force, the material can be easily deformed, bringing the charges trapped in the cavity surfaces closer together, unbalancing the electrical compensation charges, which causes an instantaneous electrical response as shown in Fig. 6 [13,43].

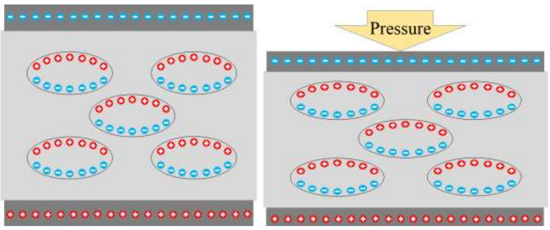

Fig. 6. Representation of electrical charges trapped in cellular polymers after electrical charging and cavity deformation by applying external pressure.

It can be seen from Fig. 6 that, after the electrical charge, the macro dipoles present in the cellular polymers are aligned in the same direction of the applied electric field. Due to the orientation of the macro dipoles, the piezoelectric effect arises when an external excitation, electrical or mechanical, is carried out perpendicularly to the surface [41, 44]. This form of polarization has led several researchers to use the PC d_{33} as the main parameter for measuring piezoelectricity in cellular polymers [41, 45]. Polypropylene (PP) stands out due to its availability and affordability when compared to other materials, as well as it can also be found in the form of cellular films. In addition, it has a high PC under ambient temperature conditions [46].

However, some studies in the literature point that these coefficients show a rapid decay when the material is subjected to temperatures above 60 °C [47,48]. Due to this low thermal stability of PP, several researchers were motivated to develop new techniques for preparing porous films with more thermally stable materials, such as PTFE and FEP. In addition to researches of new cellular film producing methods, studies have been carried out combining porous films with non-porous films have shown promising results.

D. Combination of Porous and Non-Porous Films

In 1978, Hennion and Lewiner built an acoustic transducer that used overlapping polymeric films without an intermediate layer of air. In this pioneering work, the authors used thick films with different elasticity modules for the manufacture of the transducer [49]. However, the idea of combining layers of polymers with different modulus of elasticity to obtain a better response came only years later.

In the mid-90s, Kacprzyk et al, based on the idea of Hennion and Lewiner, analyzed the piezoelectric response of structures formed with this configuration. However, Kacprzyk et al. used thin polyurethane films overlaid by polypropylene films loaded by the corona method. Although the PC's obtained by this configuration did not reach values higher than 2 pC/N, the results presented served to validate the concept [22]. In Subsequent researches with materials of different elasticity modules, Kacprzyk et al. [50] replaced polyurethane films with polystyrene films, obtaining higher PC's ≈ 23 pC/N. Also in this same approach, Gerhard Multhaupt et al. [11] managed to obtain PC's up to 35 pC/N by overlaying porous ("soft") and non-porous ("rigid") PTFE films. Although the work carried out with films of different elastic stiffness presented promising results, the irregular surface of the porous films made it impossible to uniformly deposit the electrodes, which are essential in several applications. To overcome this, more rigid metallic films were placed over the polymeric films, creating an air layer between the electrode and the porous surface of the film. This enabled electric charges to be trapped in this region, contributing to a false increase of the piezoelectric effect [51].

III. TECHNIQUES FOR PIEZOELECTRETS

The combination of porous and non-porous films proved to be effective in improving the PC. However, the adhesion between them remained challenging. That way, new techniques have been developed to solve this problem and to produce more thermally stable piezoelectrets with geometrically well-defined cavities [43]. Fig. 7 shows the composition of polymers in *ABA* structure.

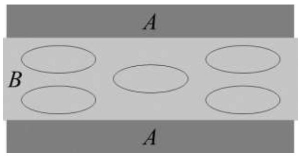

Fig. 7. Representation of the composition of porous and non-porous polymers in ABA structure.

A. Fabrication Technologies

In the first piezoelectrets with organized structures, proposed by Altafim et al. [23], there were also difficulties in adhesion among fluoropolymers. The authors built a circular structure of *ABA* type with two FEP films separated by synthetic paint. The varnish was sprayed in droplets in order to create air spaces between the FEP films and, at the same time, to ensure adhesion between them. This technique demonstrated the concept of more thermally stable polymers. However, the cavities' geometry of these piezoelectrets was still dispersed, resembling the industrially manufactured cellular polymers. In Fig. 8, the process of obtaining the piezoelectrets has been represented in detail.

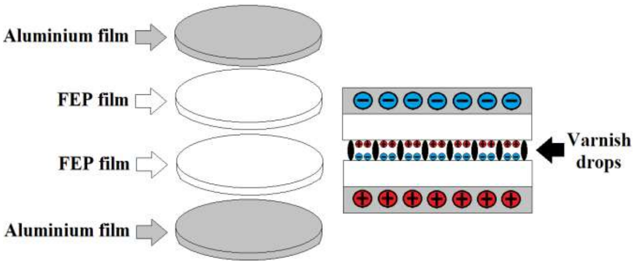

Fig. 8. Schematic representation of the process on left for obtaining the proposed electret stacking "sandwich" sheets; on right electret after being charged.

After manufacturing, these piezoelectric samples were charged by direct contact method, showing satisfactory results with PC's d_{33} up to 270 pC/N. However, the samples produced by this technique showed low mechanical resistance due to the non-stick characteristic of Teflon®-FEP. Despite this limitation, the technique demonstrated the possibility of creating electrets with acceptable piezoelectricity indexes using more thermally stable materials [52]. In order to increase the structure's mechanical resistance, Altafim et al [53,54] developed a new technique in which a molded FEP film was glued to another flat FEP film using a press specific developed for this method. It was composed of two metallic discs, one inferior and other superior, endowed with electrical resistance and independent temperature control. The lower disk had several holes and was connected to a vacuum pump that was used to deform the film placed on the metal grid, forming multiple air bubbles on it. A second film, placed over the molded film, was then presses by the upper disk against the lower one, fusing the FEP films. In Figs. 9 and 10, respectively, the device configuration and the appearance of the thermoformed sample are shown in detail, after the forming process.

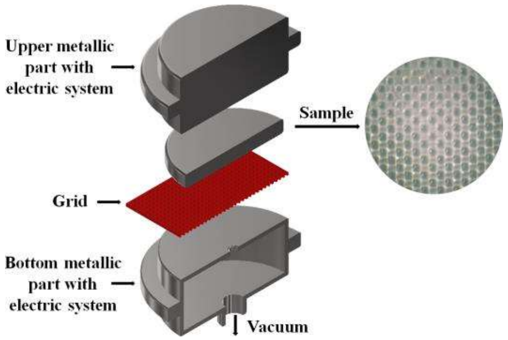

Fig. 9. Schematic representation of the process (left) for obtaining the proposed electret Stacking “sandwich” sheets; electret after being charged (right).

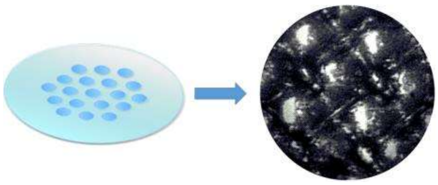

Fig. 10. Thermoformed sample in detail with homogeneous distribution of air bubbles.

Despite the good adhesion presented by this new method, the thermo-molding process caused structural damage to the bubbles, what made it difficult to control the size of the cavities [55]. However, this method showed an incremental improvement to the previous one, as in addition to allowing a regular distribution of the bubbles, it also showed greater thermal stability provided by the use of FEP. This was the first thermoformed electret ever made. After charging the samples, PC’s of the order of 500 pC/N were obtained, approximately twice as much as the previous process [52,53].

A similar method, which also allows cavities molding using the ABA structure concept, was developed by Zhang et al. [56]. The piezoelectrets proposed used a FEP film interposed by two PTFE films, where the FEP film purpose is only the adhesion between the other films. A heated metal grid at 280 ºC was pressed on the structure for an hour with a force of approximately 20 N. Fig. 11 shows the schematic of the device configuration proposed by Zhang et al.

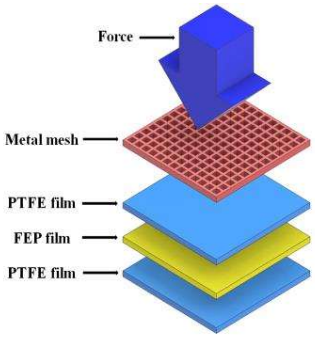

Fig. 11. Thermoformed sample in detail with homogeneous distribution of air bubbles.

The contact points between the grid and the stacked films were responsible for the fusion between them and their subsequent adhesion. The hollow regions of the grid formed air cavities and, after an hour, the grid was cooled and slowly removed. After the electrical charging, a PC greater than 1000 pC/N was measured [56]. Furthermore, Zhang et al applied the described technique above for multilayer electrets production.

It was obtained up to seven layers, interleaving PTFE and FEP films, with the outer layers being of PTFE for its higher melting point. However, the piezoelectrets resulting from this process did not have a structured organization of the cavities, nor did it present any possibility of control of the bubbles size and shape, although it had a high PC [46].

In 2007, Basso et al. [57] envisioned the possibility of applying the technique of document plastic lamination for fusion of polymeric films. Using this process, the authors produced a piezoelectret based on the three-layer system, consisting of two homogeneous FEP films separated by a perforated PTFE film with evenly distributed cavities. Initially, the cavities were manually produced in 400 µm PTFE films using a hole puncher, providing openings with a diameter between 1 mm and 1.5 mm. Smaller holes were obtained using neodymium laser pulse: YAG (neodymium yttrium aluminum garnet) with 100 µm thick PTFE films. After drilling the PTFE films, the FEP/PTFE/FEP structure was laminated at a temperature of 310 ºC, generating a thick film with well-defined homogeneous cavities. However, the PC’s obtained for the produced piezoelectrets reached a maximum value of 15 pC/N [57], well below those obtained in cellular polymers with molded bubble structures.

Altafim et al. [58] produced piezoelectrets with standardized cavities using the hot rolling technique (lamination). To control the cavities’ dimensions, the authors used a PTFE mold with a previously defined geometry between FEP films. The mold was made of a material different from the film in such a way that there was no fusion between them during the lamination, as PTFE has a higher melting point than FEP. After the FEP/PTFE/FEP arrangement was removed from the laminator, it was cooled at room temperature and the mold extracted, creating an open structure with tubular channels. The piezoelectrets produced by this technique had a PC around 160 pC/N. Based on this technique of producing thermoformed piezoelectrets, Falconi et al. [59] developed a new process in which a FEP film was precast before the lamination step. In the pre-molding stage, a hydraulic press and a metal matrix containing symmetrically spaced holes were used. After the bubble production stage, the films molded together with the metallic matrix were covered by an unmodified FEP film and was then subjected to the lamination process. After electric charging, the samples showed PC’s up to 215 pC/N [59].

Zhang et al. [60] developed a new technique to prepare piezoelectrets with standardized cavities using a rigid matrix. In the work presented by the authors, samples with structures of 3 and 5 layers were produced, where 12.5 µm FEP films were used as outer layers and a porous PTFE film with 90% porosity and 25 µm thick was used as intermediate layer. In the first stage of the manufacturing process, the porous PTFE film was molded with the rigid matrix and placed between two flat FEP films. In order to eliminate excess of air at the films’ interface, the structure was exposed to a corona electric field, causing the films to be attracted by one another by the electrostatic force. After, an oven was used to melt the films. This new manufacturing process, it was obtained piezoelectrets with PC’s d_{33} of up to 500 pC/N [60].

Table I. Summary of some of the piezoelectrets production methods.

Author / Year	**Films**	**Method**	**Description**	**Reference**
Altafim et .al. /2003	Teflon®, FEP	Cold collage	First piezoelectrets produced by the High Voltage and Measurement Group. The authors used varnish paint to promote adhesion of Teflon® and FEP films. Despite the high PC, this structure had a low mechanical resistance.	[23]
Altafim et al./2005	Teflon®, FEP	Pre-modeling of the air cavities followed by the fusion of the films	Production of the first thermoformed piezoelectrets by means of a press with heated metallic discs, connected to a vacuum pump. Improved mechanical strength, however, thermo-modeling caused structural damage to the piezoelectrets.	[53,54]
Zhang et al./2006	Teflon®, FEP, PTFE	Thermo-modeling	The authors used a heated metal grid to produce the air cavities, at the same time that the films were fused. Despite the non-uniformity of the air cavities, high PC's were obtained.	[56]
Zhang et al./2007	Teflon®, FEP, PTFE	Thermo-modeling	The authors used the same method as before, but with an overlap of several layers of PTFE and FEP.	[46]
Basso et al./2007	Teflon®, FEP, PTFE	Pre-modeling of the air cavities followed by the melting of the films	In this method, the air cavities were produced with a leak or with the use of a neodymium laser. After modeling the cavities, a laminator was used to fuse the films.	[57]
Altafim et al./ 2009	Teflon®, FEP, PTFE	Thermo-modeling	Based on the lamination technique, the authors produce piezoelectrets with controlled cavities. A PTFE mold was used to produce the air cavities.	[58]
Falconi et al./ 2010	Teflon®, FEP	Pre-modeling of the air cavities followed by the fusion of the films	The authors perform the pre-molding by means of a hydraulic press and after the modeling they use the lamination technique for the melting of the films.	[59]
Zhang et al./ 2010	Teflon®, FEP, PTFE	Pre-modeling of the air cavities followed by the fusion of the films	A rigid matrix was used to model the porous PTFE film. After modeling, flat FEP films were placed on the faces of the molded film and an oven was used to melt the structure.	[60]
Fang et al./2011	Teflon®, FEP	Pre-modeling of the air cavities followed by the fusion of the films	In this work, the air cavities were made by means of a laser. After perforation of the film, it was inserted between two flat films of FEP and again the laser was used for proper adhesion of the films.	[61]
Zhang et al./2012	Teflon®, FEP	Pre-modeling of the air cavities followed by the fusion of the films	Metallic matrices were used for the modeling of FEP films. After modeling, the films were stacked and taken to an oven to melt the films.	[62]

Fang et. al., using the concept of 3-layer piezoelectrets, developed a new methodology for their production. The samples were built essentially from FEP, with the middle layer being perforated. The holes in the central layer were made with a quadrangular geometry using a laser. After drilling, the hollow mesh was inserted between two films of FEP, which had one of its surfaces metallized. The stacked films were charged and subsequently pasted. The process of fusing the films was performed by a laser beam applied to several points around the cavities. The piezoelectrets were charged at room temperature and reached a PC of 350 pC/N [61].

In 2012, Zhang et al. produced piezoelectrets with organized microstructures with PC's in the order of 1000 pC/N. Metal plates with circular cavities with 1 mm diameter and 500 µm depth were used to mold FEP films. For the molding step, two FEP films and a soft rubber were arranged in an alternating sequence, placed between the molded metal plates and pressed at a temperature of 90 ºC for 60 seconds [62]. Subsequently, the rubber between the films was removed, obtaining the two molded films, which were attached and fused together in an oven at 290 ºC for 10 minutes. For 3-layer structures, a flat film of FEP was inserted between the molded films, repeating the fusing process [62].

Despite the aforementioned piezoelectrets use more thermally stable polymers, presenting stability above 80 ºC [18, 58,63-65]; continuous efforts have been made in order to increase the working temperature of these materials. In order for the stability to be improved, chemical and thermal treatments of the films forming the piezoelectrets have been elaborated. *Table 1* has a brief description of all the aforementioned piezoelectrets manufacturing methodologies.

B. Improvement Techniques

With the need to increase the temperature operating range and porosity of piezoelectrets, in order to improve the charge trapping and consequently increase the PC, several techniques were developed by researchers as previously mentioned. Among these techniques, two types stand out: chemical treatment and heat treatment.

a. Chemical treatment

In 2004, Rychkov et al. [66] showed the influence of chemical modifications on the surface of PTFE films. In this work, the authors used phosphorus trichloride (PCL_3) to alter the chemical composition of the PTFE surface using chemical nanotechnology based on Molecular Layer Deposition (MLD). After the surface chemical modification, water vapor was used to replace the chlorine ions with OH groups, as the thermal stability of the surface potential in PTFE films is correlated to the concentration of OH groups [66,67]. In 2007, Rychkov et al. [68] used the same modifying agents as the previous work to change the surface of low density polyethylene (LDPE). The results obtained were similar to those found in the previous study, however, the potential superficial relaxation in the PTFE depends on the polarity of the charge. Only positive charges showed an increase in thermal stability, whereas for LDPE this behavior does not depend on the signal of the charge stored in the electret. In Fig. 12, it is shown the results obtained in this experiment of the surface's potential behavior due to the increase in temperature by the treatment performed on PTFE films on left, and on LDPE films on the right.

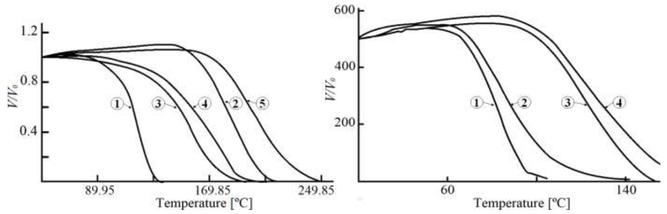

Fig. 12. Surface potential (left) of untreated and treated PTFE films charged with positive charges; and surface potential (right) of untreated and treated LDPE films charged with both polarities. Source: Adapted from RYCHKOV et al., 2004, p. 278. [66],and p. 462. [68].

The curves shown on the right were produced with positive corona charging method: curve 1 shows the behavior of the untreated film; curve 2 shows the behavior of the water-based treatment; curve 3 is related to the superficial modification caused by treatment with PCL_3; curve 4 expresses the behavior of the sample treated with PCL_3 followed by hydration with water vapor; and curve 5 represents the sample from curve 3 followed by a water treatment. From the analysis of the graph in Fig. 12 (left) (PTFE), it was found that the treatment was efficient, showing greater stability when water is used. Note from Fig. 12 (right) (LDPE) that there is little difference between curves 1 and 2, which are untreated samples charged with positive and negative charges. The samples represented by curves 3 and 4, which were submitted to the chemical treatment process and charged with both polarities, have a noticeable improvement in charge retention.

In 2009, An et al. [85,86] reported studies on the superficial treatment of PP-based piezoelectrets. The two studies presented very similar results although different methods were used. In the first work, it was used a treatment based on fluorine gas in which PP films were placed in a stainless steel container with an outlet for an external electric oven. A mixture of fluorine and nitrogen gas was inserted into the vessel at a pressure of 225 mBar for 30 minutes. The temperature during the treatment was approximately 55 ºC. After the reaction, the mixture was removed with the aid of nitrogen. After this treatment, the films were expanded and later charged with the negative corona method. Fig. 13 shows the results obtained in this experiment.

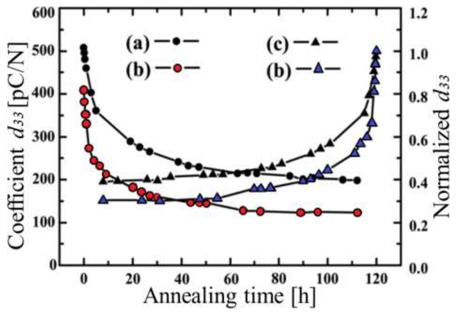

Fig. 13. Isothermal decay at 70 ºC: curve (**a**) and (**c**) treated samples; (**b**) and (**d**) untreated samples. Adapted from AN et al., 2009, p. 3. [69, 70].

The values represented in Fig. 13 correspond to the average of 5 samples. It can be seen that there was a gain in the treated samples compared to the untreated ones. This improvement was conditioned by greater thermal stability of charges stored in deep traps. Another interesting factor caused by the proposed treatment is the improvement in piezoelectric activity, related to the decrease in the elasticity modulus. In the second work, the PP film was oxidized by a solution of chromic acid for a period of two hours. Then, the film was exposed to a treatment with hydrofluoric acid for another six hours at room temperature. At the end, the samples were washed with deionized water and air dried at temperatures below 50 ºC. The results obtained by this study were very similar to those presented in the previous work. Fig. 14 shows the results obtained of the PC's behavior of the untreated samples and with the chemical treatment, respectively.

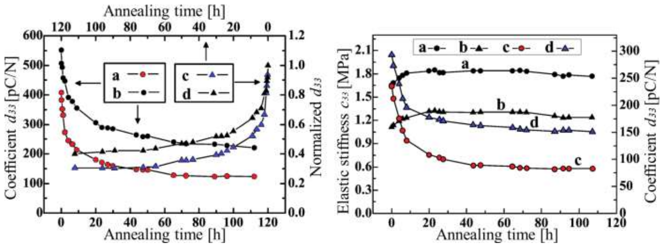

Fig. 14. Isothermal decay at 70 ºC (left): curve (**a**) and (**c**) untreated samples; (**b**) and (**d**) treated samples; and (right): change in elastic stiffness (**a**) untreated samples and (**b**) treated samples. Curves (**c**) and (**d**) represent the PC of the untreated and treated samples, respectively. Source: Adapted from AN et al., 2009, p. 803. [69, 70].

In 2012, Rychkov et al. [71] used the piezoelectric production technique presented in 2009 by Altafim et al. [58], with which it is possible to produce piezoelectrets with open channels, what facilitates subsequent chemical treatment. In this work, the authors used LDPE to produce the piezoelectrets and, subsequently, phosphoric acid (H_3PO_4) to perform the chemical treatment. The samples were submerged in the acid for twenty-four hours at a temperature of 60 ºC. After this period, they were washed with water and subsequently charged. Fig. 15 shows the results obtained in this experiment. It can be seen from it that the chemical treatment with an element of an acid character promotes an increase both in thermal stability and in the PC of the material.

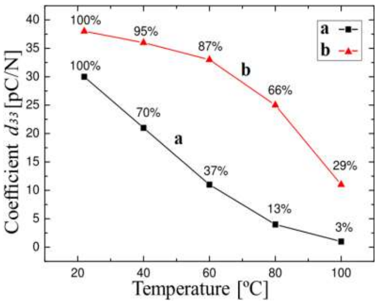

Fig. 15. PC temperature-dependent in LDPE piezoelectrets curves: (**a**) untreated samples; (**b**) treated samples. Source: Adapted from RYCHKOV et al., 2012, p. 124105-3. [71].

b. Heat treatment

Heat treatment is another technique applied to increase the thermal stability of piezoelectrets. In 2010, Qiu et. al [72], used porous and non-porous PTFE charged films and subjected them to a heat treatment cycle. These films were heated to a temperature of 320 ºC for an interval of two minutes and subsequently cooled in liquid nitrogen. As a result, it was observed that the non-porous PTFE films showed a reduction in their thermal stability, whereas the porous films showed an improvement. Fig. 16 shows the results obtained in this experiment.

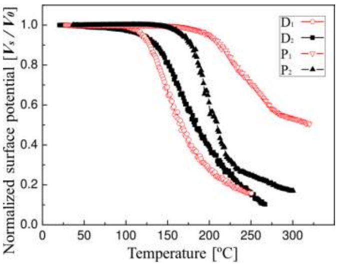

Fig. 16. Decay of surface potential for porous and non-porous PTFE. Source: Adapted from QIU et al., 2010, p. 2. [72].

From the graph in Fig. 16, the letter D indicates non-porous films and the letter P porous films. The black curves represent the untreated films and the red curves the treated ones. Curve D_1 shows the decreasing of the stability of the non-porous film as a result of slightly reduced crystallinity by the treatment. On the other hand, this treatment increased the crystallinity of the porous film, as seen in curve P_1.

Regarding the heat treatment of piezoelectrets already finished, it is generally carried out in two different ways: annealing and charging at high temperatures. In the annealing technique, the samples are charged and subsequently heated to temperatures previously determined for certain periods of time. This technique was used in several works available in the literature [60,64-65,73], however, its use promotes a reduction in the PC. The second technique, however, where piezoelectrets are charged at elevated temperatures [46,58,61], shows an increase in their thermal stability. An advantage in relation to the annealing technique is that there is no decreasing in the initial PC when charging at high temperatures. In Fig. 17 it is shown the results obtained by Fang et. al. [74] comparing the difference between annealing and charging at high temperatures.

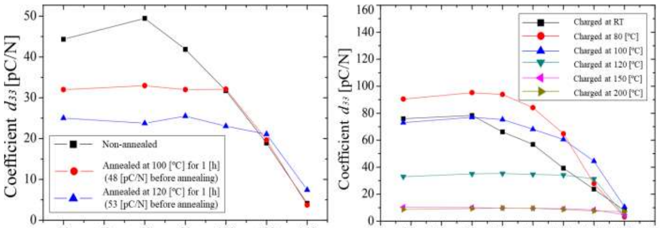

Fig. 17. PC d_{33} of annealed and non-annealed samples (left) of polyethylene naphthalate (PEN); and (right) decay of PC d_{33} as a function of temperature. Source: Adapted from FANG et al., 2010, p. 1083. [74].

It can be seen from Fig. 17 (left) that there was a reduction in the initial PC of the annealed samples, and the thermal stability maintained until the annealing temperature was reached in both of them. This shows that the annealing technique limits the stability for the temperature used in the treatment. At temperatures above annealing, decay begins in the PC. The lower PC with annealing is explained by the tendency of electrical charges stored in shallow surface traps to be released by heating, concentrating more charges in deeper traps, thus allowing the annealed samples to be subjected to higher temperatures. This limits the annealing temperature, without subsequent loss of stored charges. It can be seen from Fig. 18 (right) that charging at elevated temperatures also improves the thermal stability of the piezoelectrets. However, the heating temperature cannot exceed the glass transition temperature of the material. If it exceeds this temperature, it would cause permanent deformations in the piezoelectrets.

IV. NEW PIEZOELECTRETS PRODUCED BY 3D PRINTING

3D-printing first requires a representation of the object to be replicated or created – which is modeled using a computer-aided design (CAD) software. Furthermore, material specific 3D-printing parameters such as temperatures, velocities and filling patterns and densities need to be defined and set in the software that controls the printing process. For electro-active polymers, the 3D-printing process is similar for the conventional polymer passive usage.

As the electrical charging, resonance frequencies and resulting piezoelectricity depends on the cavity dimensions [75,76], the main advantages of the 3D-printing process is the control of the cavities' geometrical parameters, such as shape, height, thickness and spatial density – as it allows the fine tuning of the resonance frequency – as well the repeatability and scalability of the fabrication process. Different polymers can be used in this process such as ABS, poly (vinyl alcohol) and polylactic acid. Controlled voided structures suitable for piezoelectrets have been produced with 3D printing technology [77], although it was used in the fabrication of plastic molds employed on the preparation of polydimethylsiloxane structures.

Proposed by Assagra et al [24], a very promising approach for preparing ferroelectrets with well-defined cavities utilizing 3D printer technology with an alternative method of fabrication produced ABS piezoelectrets with well-controlled cavity geometries, being ABS chosen due its electrical properties [78,79]. The procedure consisted of printing two separate thin films, one containing ring-shaped ridges on a flat surface and the other one being completely flat. The ABS films 3D printed were then joined together to form a 2-layer sandwich with internal cavities. The width and length of each sample was 40×40 mm^2. The flat film had thickness of 100 μm, while the other had a total thickness of 200 μm – one flat surface of 100 μm and the ring-shaped ridges upon it with 100 μm height each, as shown in Fig. 18, and images of the circular voided structure and the finished piezoelectret sample. With metal electrodes adhesives stuck on both samples surfaces, after electrical charging with a DC voltage of 4.5 kV, the resulting structure presents a piezoelectric behavior similar to that of typical ferroelectrets, showing a PC around 100 pC/N.

The PC 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 stabilization. However, the use of the ABS polymer with its low thermal charge stability have resulted in electrically rather unstable ferroelectrets. After exposure to temperatures up to 85 °C, a 30% drop in PC was observed. This thermal stability is higher than those observed on chemically treated polyethylene (PE) piezoelectrets [71]