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Biodegradable cellular polylactic acid ferroelectrets with strong longitudinal and transverse piezoelectricity

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ABSTRACT

Polymers with electrically charged internal air cavities (ferroelectrets) reveal a pronounced piezoelectric response and are regarded as soft electroactive multi-functional materials. This work presents preliminary results on the preparation and piezoelectric effect of ferroelectrets based on the polylactic acid (PLA) polymer. A distinctive feature of the manufactured films is that they are biodegradable. After a microstructure modification of carbon dioxide (CO_2) foamed PLA sheets by hot-pressing treatment and corona polarization, these cellular films reveal large piezoelectric d_{33} and d_{31} responses in both quasi-static and dynamic modes. For freshly charged films, the maximum quasi-static piezoelectric coefficients are about 600 pC/N (d_{33}) and 44 pC/N (d_{31}) for a relatively thick film of 360 μm and a nominal porosity of about 60%. During the first 20 days after polarization, the piezoelectric activity decreases by half compared to the primary value, but then remains almost unchanged for a long time. Due to an already established inherent biocompatibility of PLA polymers, these eco-friendly ferroelectrets can be potentially used in various biological applications such as biosensors and microenergy harvesters embedded in tissue and artificial muscles.

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Ferroelectrets or piezoelectrets belong to the class of electroactive materials that possess a cellular structure and can convert mechanical energy into electric energy and vice versa.[1,2] Such materials are used in various smart arrays to measure or generate electrical or mechanical deformation signals, e.g., in sensors, actuators, energy harvesters, etc.[3,4] Initially, mostly nonpolar cellular films exhibit a strong piezoelectric effect only after symmetry breaking by proper poling in strong electric fields. Piezoelectricity, thereby, originates from engineered dipoles/polarization induced by the poling process.

Various ferroelectrets with a cellular structure have been reported in the literature. These are based on polypropylene (PP),[5–7] polyethylene(PE),[8] polyethylene terephthalate (PETP),[9] polyetherimide (PEI), polyether ether ketone (PEEK),[10] cyclo-olefin polymers (COP)[11] and their copolymers (COC),[12] and fluorocarbon polymers.[13,14] Recent advances in cellular materials used as ferroelectrets are reported in several comprehensive reviews.[15,16] Among these materials, cellular PP is

the first and most extensively studied ferroelectret showing longitudinal piezoelectric d_{33} coefficients on the order of a few hundred pC/N.[5–7] However, the transverse piezoelectric d_{31} coefficient of PP is limited to approximately 2 pC/N.[17] The same fact applies to the aforementioned ferroelectrets, except fluorinated polyethylene propylene (FEP) films with a parallel tunnel structure.[18–20] Nevertheless, a sizable longitudinal and transverse piezoelectric effect in the same material is highly desirable due to its larger scope of applications. Since all these materials are carbon based and fabricated from fossil fuels, they are long-lived and do not comply with eco-friendliness, biocompatibility, and biodegradability, all necessary to reduce the negative impact on the environment.[21,22]

Biodegradability, however, has become an important issue for the modern generation of biosensors.[23] In some urgent and short-term medical applications, e.g., healing of wounds or bones, where the functionality of the sensor is only required for a limited time, the

implantation of biodegradable sensors can eliminate the need for a follow-on operation. It has long been discovered that a number of bio-polymers, including polylactic acid (PLA), show predominantly shear piezoelectricity with a maximal piezoelectric constant of 10 pC/N.[24,25] Such piezoelectricity can only be detected when PLA is in a crystalline state, and the origin of piezoelectricity is determined by the internal rotation of the polar group CO–O.[25] On this basis, a first fully biode-gradable piezoelectric pressure sensor based on PLA was developed to control important physiological forces.[26]

　　This Letter presents results on the preparation and the piezoelec-tric effect of ferroelectrets made from cellular PLA. The films fabri-cated are the biodegradable ferroelectrets featuring both significant longitudinal and transverse piezoelectric activities. Figure 1 illustrates the life cycle of a PLA ferroelectret material, and the present work is focusing on the period from microstructure modification of the PLA foam sheets to characterization of the PLA ferroelectrets. Note that the high piezoelectric activity discovered here is the result of a unique combination of space-charge electrets and mechanical properties of cellular PLA films and is not related to the inherent low piezoelectric-ity of crystalline PLA, which, therefore, can be completely ignored in this study.

　　The initial raw material used in this study is a modified PLA resin (Guangzhou Bio-plus Materials Technology Co., Ltd., Bio-plus 301H)[27] with a density of 1240 kg/m^3 and a melting point ranging from 165 °C to 175 °C. The resin was physically foamed with carbon dioxide (CO_2) in the melt by utilizing an industrial foaming produc-tion line, resulting in PLA foam sheets with a thickness of 1.3 mm and an area density of 0.134 kg/m^2, corresponding to a nominal porosity of 92%. In order to render the PLA foams piezoelectric, i.e., to fabricate the ferroelectrets, modification of the microstructure by pressing at elevated temperatures [Fig. 2(a)] and polarization by corona charging [Fig. 2(b)] were carried out. As a first step, the PLA foam sheets were

clamped between two metal plates and pressed for 4 min at 50 °C at a pressure of 2 MPa using a Platen vulcanizing press machine to achieve the desired thickness, which was defined by the height of suited spacers [see Fig. 2(a)]. Thereafter, the PLA films with the supporting metal plates were cooled down to room temperature by using a cold press machine to stabilize the micro-structure. The thickness of the film during hot-pressing at 50 °C and cooling was controlled by using four pieces of brass sheets with specified thicknesses placed around the samples. Figure 2(c) displays the achieved porosities of the modified PLA foams, determined by the weight as a function of thickness of the resulting films. The SEM images of cross sections of an original PLA foam sheet (sample 1) with a thickness of 1.3 mm and a modified cel-lular PLA film with a thickness of 360 μm (sample 2) are depicted in Fig. 2(d). It should be noted that when the virgin sheet was hot pressed, its thickness decreased and, at the same time, the nominal porosity of the pressed films decreased to 40% for a thickness of 200 μm. The shape of the pores also undergoes alterations during the hot-pressing process. For example, the original PLA film contains a large number of elliptical voids, the height of which is about 150 μm with a wall thickness of several micrometers. Upon pressing this film to a thickness of about 360 μm [Fig. 2(d), sample 2], the elliptical cavi-ties flatten. The average thickness of the air voids decreases to about 30 μm. Such a modification of the porous shape can, in principle, not only improve the charging efficiency of the cellular structure[28,29] but also reduce Young's modulus, in particular in the direction of the film thickness, thus ultimately leading to a significant increase in the d_{33} piezoelectric response of the film.[30,31]

　　At the next stage of preparation, the obtained PLA films were polarized at room temperature in a corona charging setup by mount-ing the modified non-metallized film on a metal plate [Fig. 2(b)]. The corona tip voltage and charging time are –25 kV and 5 min,

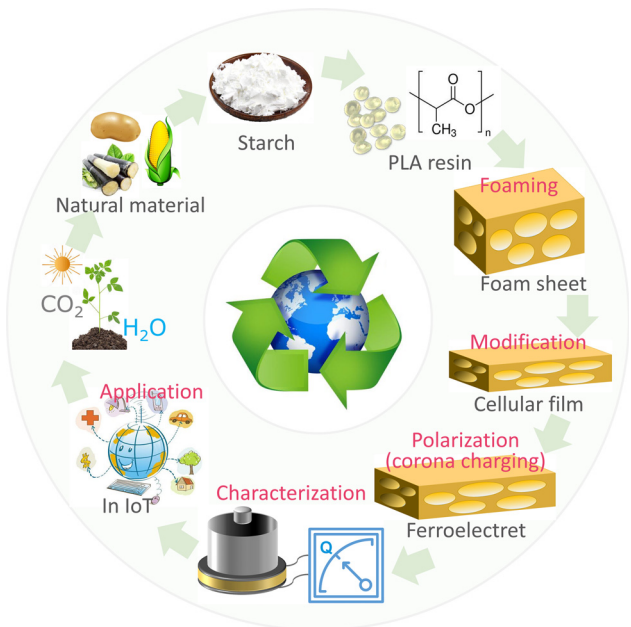**FIG. 1.** Life cycle of a biodegradable PLA ferroelectret.
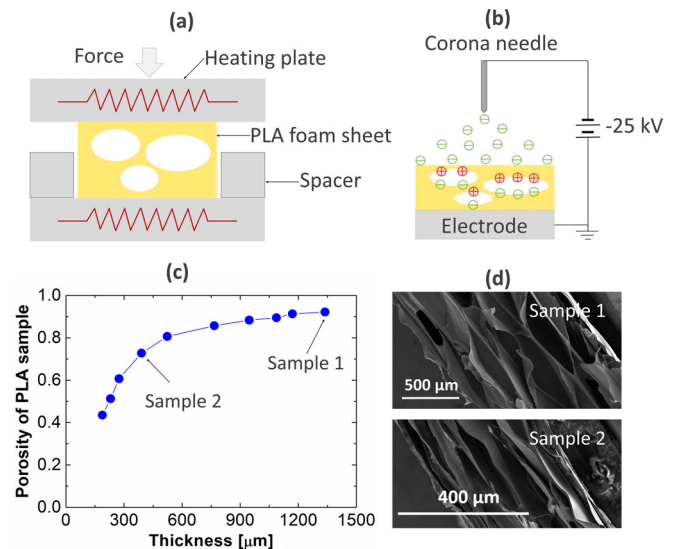

FIG. 2. Schematic diagram of the preparation process of PLA ferroelectrets: (a) hot pressing treatment, (b) corona charging process, (c) porosity of PLA samples as a function of film thickness, and (d) SEM images of cross sections from the original PLA foam (sample 1) and hot-pressed PLA film (final thickness: 360 μm) (sample 2).

respectively. The distance between the corona tip and the sample surface was 5 cm. After charging, both sides of the samples were metallized with 100 nm thick aluminum electrodes by thermal vapor deposition. Such samples were used to study their piezoelectric characteristics.

In order to determine the quasi-static and dynamic d_{33} coefficients, circular samples with an electrode diameter of 20 mm were used. The quasi-static piezoelectric d_{33} coefficients were determined by the application of a defined mass $m = 100$ g to the sample. Thereby, the charge Q integrated for 10 s was recorded by means of an electrometer (Keithley, Model 6514). In this way, the d_{33} coefficient is given by

$$d_{33} = \frac{Q}{mg} = \frac{\sigma_0}{p_s}, \quad (1)$$

where Q denotes the amount of charge induced on the electrodes, g the acceleration of gravity, $\sigma_0 = Q/A$ the induced charge density, and $p_s = mg/A$ the stress applied to the sample of electrode area A. In this work, $p_s = 3.1$ kPa for the utilized electrode area is used.

The experimental d_{33} coefficients obtained for PLA transducers of different thicknesses are compared in Fig. 3 with those reported for other conventional cellular polymers, including PP, PETP, and COP. Among those, the PP polymer is often referred to as a benchmark for ferroelectrets. The PLA transducers were charged one day before measurement, and each experimental d_{33} value shown in Fig. 3 is the result of averaging over 10 measurements performed on the same sample with a pitch of 1 min. All PLA ferroelectrets obtained exhibited a strong piezoelectric response with a maximum value of 600 pC/N observed for the 360 μm thick sample. As can be seen in Fig. 3, this maximum value significantly surpasses typical values of d_{33} coefficients reported for transducers of thicknesses exceeding 100 μm made from other cellular polymers. In comparison, the well-known piezoelectric polymer poly(vinylidene fluoride) (PVDF) has a d_{33} coefficient of only about -25 pC/N.[1,15]

Note that a similar peaked dependence of the d_{33} coefficient on the thickness is also observed for other cellular ferroelectrets.[9,30,31] The reason for such a peaked function is commonly attributed to the variation of the elastic modulus for different thicknesses, which results from a compromise of the void wall thickness, void size, and void shape.[6,30–33] Additional studies on the mechanical and charging properties are necessary to explain the observed peak for particular PLA
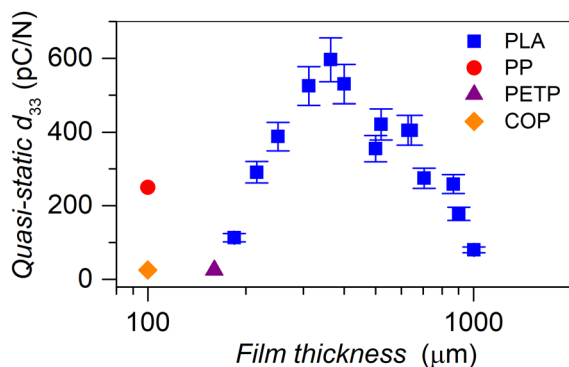
structures. This, however, is beyond the scope of this Letter and will be reported in forthcoming research. Instead, the dynamic longitudinal and transverse piezoelectric characteristics of PLA samples, as well as their temporal stability, are investigated.

To study the dynamic longitudinal piezoelectric d_{33} coefficient, a seismic mass m_s is placed onto the sample. An electrodynamic shaker (B&K 4809) was utilized to accelerate the sample and seismic mass sinusoidally for various accelerations a, thereby generating a charge Q on the electrodes. The shaker was driven by an audio analyzer (dScope Series III) through a buffer amplifier (B&K 2706). When the gravitational acceleration g in Eq. (1) is substituted by the acceleration a, this equation can also serve to determine the dynamic d_{33} coefficient. The actual acceleration applied to the device was measured using an accelerometer (B&K 4332) placed directly onto the shaker. At the same time, the produced charge was amplified by a charge amplifier (B&K 2635) and then measured using an audio analyzer. More details about the experimental setup can be found elsewhere.[34]

As an example, the experimental results obtained for various m_s values ranging from 20 g to 160 g for a 360 μm thick sample are displayed in Fig. 4(a). One can observe that the PLA transducer displays remarkable and flat frequency responses up to the resonance region located between 100 Hz and 200 Hz. Based on a previously developed analytical model,[35] the resonance angular frequency ω_r at which a maximum is observed in Fig. 4(a) for a specified seismic mass can be expressed as follows: $\omega_r = \omega_0 \sqrt{1 - \zeta^2}$, where

FIG. 3. Comparison of the static piezoelectric d_{33} coefficients of PLA films of different thicknesses developed in this work and previously reported cellular ferroelectrets.[5–11] All PLA samples were measured at room temperature.
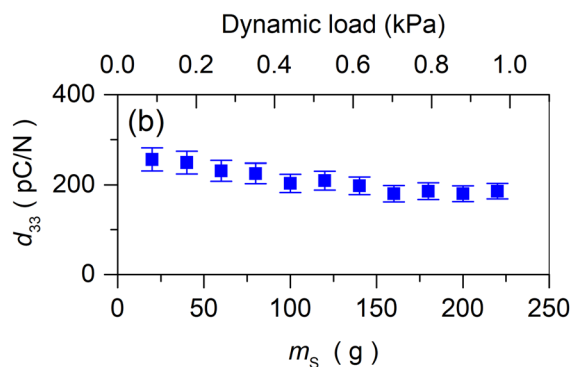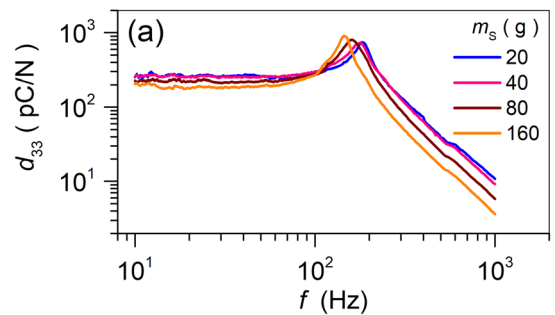

FIG. 4. (a) Dynamic piezoelectric d_{33} coefficients for the 360 μm thick PLA transducers vs frequency for different seismic masses m_s as indicated. (b) d_{33} coefficient at a fixed frequency of 20 Hz vs seismic mass and corresponding dynamic load.

$$\omega_0 = \sqrt{\frac{Y_3 \, A}{t \, m_s}} \qquad (2)$$

is the eigenfrequency of the PLA transducer, Y_3 its Young's modulus in the thickness direction, A and t the sample area and thickness, respectively, and ζ the damping ratio. In particular, Eq. (2) explains the shift of the maxima, displayed in Fig. 4(a), toward a lower frequency for larger m_s. In this assessment, it is also necessary to take into account the dependence of Young's modulus on stress.

For the same specimen, the dynamic d_{33} coefficients at a fixed frequency of 20 Hz are shown in Fig. 4(b) as a function of seismic mass m_s and the corresponding dynamic loads. It can be observed that an increase in the dynamic mechanical load to approximately 1 kPa only slightly weakens the piezoelectric d_{33} response, which over the measurement range gradually decreases from about 250 pC/N to 200 pC/N. It should be noted that the obtained values for the dynamic d_{33} coefficients are considerably smaller than the static ones shown in Fig. 3. However, this seems to be a common property of ferroelectrets, where the dynamic piezoelectric coefficients can reach only half of the static ones, mainly due to the difference between the static and dynamic elastic moduli.[36,37] Our experiments show that, regardless of the thickness of the samples, all the PLA transducers exhibit flat low-frequency dynamic piezoelectric responses with amplitudes also about one half of their quasi-static d_{33} values (see Table I).

In the following, we report on the transverse piezoelectric activity of the cellular PLA ferroelectrets. For measuring the quasi-static transverse piezoelectric d_{31} coefficients, the samples were cut into stripes with an electrode length l and width w of 30 mm and 10 mm, respectively. A tensile tester (KJ-1065A) was utilized to stretch the sample in the length direction with a static force F. The resulting induction charge Q on the electrodes was recorded using an electrometer (Keithley, Model 6514). In this approach, d_{31} is determined as follows:[19]

$$d_{31} = \frac{Q}{F} \frac{t}{l}, \qquad (3)$$

where t is the thickness of the sample.

Striped PLA samples were clamped in a holder at their two ends to investigate the dynamic transverse piezoelectric properties. A shaker (B&K 4809) driven by a PULSE Analyzer (B&K 3560C) and amplified by a power amplifier (B&K 2713) was used to excite the sample. The stretching force was measured using a built-in force transducer (B&K 8200). First, the force signal was amplified via a Conditioning Amplifier (B&K 2692) and then recorded using the PULSE Analyzer.

TABLE I. Piezoelectric coefficients for selected PLA foams.

Thickness μm	Static d_{33} pC/N	Dynamic d_{33} at 20 Hz pC/N	Static d_{31} pC/N	Dynamic d_{31} at 20 Hz pC/N
250	388	181	22	4.8
360	596	277	44	6.1
400	530	252	25	3.2
520	420	210	28	3.8
630	405	179	39	5.7

The charge generated by this process was recorded using the same PULSE Analyzer.

The obtained experimental d_{31} coefficients for the selected PLA transducers are listed in Table I, while the frequency responses of the particular transducers are depicted in Fig. 5. The results show that the transverse quasi-static piezoelectric coefficients of PLA foams are significant, exceeding the d_{31} response of cellular PP by more than a factor of 10. However, the obtained values for the dynamic d_{31} coefficients are much smaller than those for the static ones and only amount to about 20 percent thereof (see Table I). As in the case of the longitudinal piezoelectric response, it can be assumed that the main reason for this discrepancy is also associated with the large difference between the static and dynamic elastic moduli, but, in particular, in the transverse direction. The dynamic modulus of elasticity can decrease with decreasing frequency,[37,38] while the piezoelectric coefficient, on the contrary, should increase in this case.[30] An increase in the dynamic coefficient towards low frequencies is clearly seen in Fig. 5. Therefore, the difference between the dynamic coefficient measured at a frequency well below 20 Hz and the static one may be significantly less than that shown in Table I.

Results of the temporal decay of the quasi-static piezoelectric d_{33} coefficients, obtained at room temperature (T = 22 °C ± 5 °C) and in an ambient atmosphere with a rather high average humidity (RH = 72% ± 2%, Shanghai, October, 2019–March, 2020)[39] for two selected PLA ferroelectrets, are shown in Fig. 6. For both samples, their piezoelectric coefficients indicate a fast decay in the first few days after charging. However, after approximately 20 days of storage under ambient conditions, the coefficients stabilize and remain virtually unchanged over the next 130 days. Quantitatively, d_{33} decreases to about 50% of the initial value during the first 20 days for all investigated PLA ferroelectret samples, regardless of their thickness. Note that the residual d_{33} coefficient after 150 days of storage is still very high and, depending on the thickness of the samples, amounts from 100 pC/N to 300 pC/N. Unfortunately, almost all cellular ferroelectrets demonstrate a partial degradation of their piezoelectric characteristics in course of time.[40–42] As previously reported for other systems, the use of additional processing treatments, including charging and pre-aging at elevated temperatures,[43–45] may help to improve the long-term piezoelectric stability of PLA ferroelectrets. It is known for ferroelectrets, in general, that their resistance to fatigue and aging is
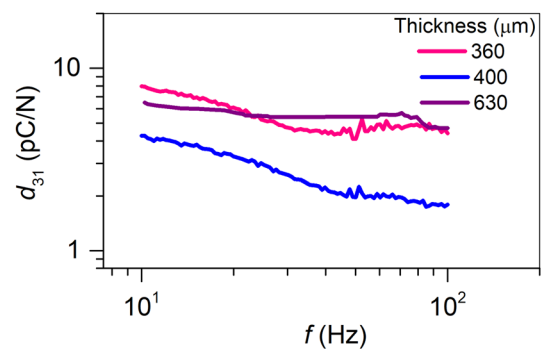

FIG. 5. Dynamic piezoelectric d_{31} coefficient as a function of frequency for PLA ferroelectrets of various thicknesses, as indicated. The measurements were performed utilizing a dynamic force of 0.2 N.
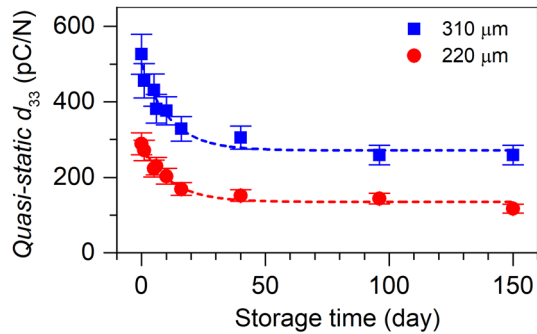
FIG. 6. Temporal decay of the quasi-static d_{33} coefficient at room temperature ($T = 22\,°C \pm 5\,°C$) and in an ambient atmosphere (RH $= 72\% \pm 2\%$, Shanghai, October, 2019– March, 2020)[39] for two PLA ferroelectrets of different thicknesses as indicated. The samples were polarized under the same conditions, with a corona tip voltage of -25 kV for 5 min. Dashed lines are given as guides to the eye.

mainly determined by two factors: their mechanical and their charge storage stabilities. In the present case, a temporary decrease in piezo-electricity can be associated, first of all, with the instability of the remanent charge and not with the mechanical degradation of the cellular structure. However, further studies are needed to evaluate these properties in detail.

In conclusion, this work reports an approach to fabrication of high performance biodegradable ferroelectrets from PLA resins, including formation of cellular structures and build-up of remanent polarization. Cellular PLA films with high charging capability were fabricated by physical foaming with CO_2 and microstructure modification by hot-pressing. A series of PLA films with different thicknesses and corresponding nominal porosity between 90% and 40% was prepared and investigated. After polarization in an external electric field, the resulting structures exhibit high piezoelectric d_{33} and d_{31} coefficients in both quasi-static and dynamic modes. The high piezoelectric activity is the result of a unique combination of space-charge electret and mechanical properties induced by the cellular structure of PLA foams. For freshly polarized films, the maximum quasi-static piezoelectric coefficients are 600 pC/N for d_{33} and 44 pC/N for d_{31}, observed for a 360 μm thick film with a nominal porosity of about 60%. Piezoelectric activity degrades to half its initial value during the first 20 days, but then remains unchanged for the next 130 days. Due to the biocompatibility of PLA, these ferroelectrets can be potentially used in a variety of biological applications, such as biosensors embedded in tissue, micro-energy harvesters, and artificial muscles. In addition, the developed PLA transducers retain most of the advantages of conventional polymer ferroelectrets, such as flexibility and good processability, and, at the same time, are environmentally friendly and biodegradable.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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