Fully Printed Piezoelectric Polymer Loudspeakers with Enhanced Acoustic Performance

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Piezoelectric polymer loudspeakers have advantages like lightweight, flexibility, simple structure, and small volume, which make them favorable for a variety of applications. Herein, such loudspeakers are fabricated by screen printing the bottom and top electrodes [poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate), PEDOT:PSS] as well as the piezoelectric polymer layer (poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE)), in between on paper substrates. The dielectric properties of the printed loudspeakers are studied with dielectric spectroscopy. Thanks to the self-healing process during poling, the samples are successfully poled to saturation in spite of their large area of up to 300 cm². The dependence of the acoustic output on remanent polarization and the active area of the piezoelectric layer is investigated. A sound pressure level (SPL) of about 91 dB at a distance of 1 m is obtained with array samples of five rectangular units (10 × 6 cm² in area each). In particular, samples with two loudspeaker arrays printed, respectively, on both surfaces of the paper substrates are prepared, and a further increase of 6 dB in SPL is achieved when the two loudspeakers are driven in phase. The results not only deepen the understanding of fully printed piezoelectric polymer loudspeakers but also realize an SPL much higher than that reported in previous studies.

1. Introduction

Advanced sensors and actuators are essential for smart systems that enable a higher quality of life in modern societies. Piezoelectric materials transform mechanical variables (displacement or force) into electrical signals (charge or voltage) and vice versa, suitable for a large range of existing or conceivable applications. Strong piezoelectricity in poly(vinylidene fluoride) (PVDF) was first reported by Kawai in 1969.[1] Compared with inorganic materials, polymers have several outstanding advantages such as lightweight, flexibility, and easy or moderate processing conditions. Therefore, research and application of piezoelectric polymers have attracted a lot of attention, although their piezoelectric sensitivity still cannot compete with that of some of their ceramic counterparts.[2–4] Nowadays, PVDF-based piezoelectric polymers have been widely explored for memory devices, energy harvesters, flexible electronics including sensors and actuators, etc.[5–11] Based on the inverse piezoelectric effect, piezoelectric materials vibrate under alternating driving electric field. Thus, piezoelectric materials can be used for designing electroacoustic devices such as loudspeakers. Loudspeakers are essential component parts in multimedia systems. Traditional moving-coil loudspeakers (also known as dynamic loudspeakers) are still commonly used, because they are capable of producing desired sound pressure levels (SPLs). However, dynamic loudspeakers have some limitations. They have a relatively complex structure, which makes them bulky and hinders their applications. Furthermore, the magnetic radiation and interactions between the coil and magnet are also limiting factors in certain applications. In comparison, piezoelectric loudspeakers have a simple sandwich structure, i.e., two electrodes and a piezoelectrically active layer in between. Direct electromechanical transformation is realized, owning to the inverse piezoelectric effect of the active layer, without the need for a magnetic field.

So far, a number of studies have been dedicated to the acoustic performance of PVDF in the audio frequency range. Already in 1975, Tamura et al. studied flat and bent PVDF films for loudspeaker applications.[12] Ohga proposed a bimorph structure consisting of a PVDF layer pasted on a polyester film substrate as a loudspeaker with multiresonances.[13] In this case, the PVDF layer operates as an actuator, which brings the entire bimorph to vibrate as a membrane. Lee et al. studied the acoustic performance of PVDF films with electrodes of different materials.[14] Bailo et al. theoretically and experimentally investigated the acoustic response of bimorphs consisting of two PVDF layers.[15]
Later, layered structures of PVDF films pasted on fabrics\cite{16} and a polyethersulfone film\cite{17} were investigated for potential applications in active noise control and in flexible displays, respectively. These studies demonstrated the usefulness of PVDF as piezoelectric loudspeakers. However, PVDF forms the nonpolar $\alpha$-phase with conventional preparation procedures such as solution casting and melt cooling. A stretching process is usually applied to turn the $\alpha$-phase PVDF into $\beta$-phase, which increases the cost and prevents the application of PVDF.

More recently, printing techniques have been utilized in the preparation of piezoelectric polymer devices. Printing is a convenient method for low-cost mass production. It is highly flexible toward selecting different printing patterns and substrates. The copolymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) is suitable for printing because it forms the ferroelectric $\beta$-phase directly from the solution. Several groups developed all-printed piezoelectric polymer devices as sensors and actuators.\cite{18–21} Hübler et al. reported, for the first time, piezoelectric P(VDF-TrFE) loudspeakers mass printed on conventional paper substrates.\cite{22} A SPL up to 80 dB was achieved with the fabricated loudspeakers, demonstrating the possibility of producing thin and flexible loudspeakers on paper substrates. In this article, fully printed piezoelectric polymer loudspeakers with significantly higher SPLs are reported. Dielectric properties of the printed loudspeakers were studied with dielectric spectroscopy. Hysteresis loops of the samples were determined by means of a homemade sawyer–tower circuit. The influence of remnant polarization and the area of the piezoelectrically active layer on the acoustic output of the loudspeakers were examined. It is found that array samples of five rectangular loudspeaker units (10 $\times$ 6 cm$^2$ in area each) are able to emit an SPL of about 91 dB. In addition, samples with two loudspeaker arrays printed respectively on both surfaces of the paper substrates were prepared, and a further increase of 6 dB in SPL was achieved.

2. Results and Discussion

2.1. Morphology and Phase Composition

All samples were prepared using the screen printing technique. The thickness of the printed layers depends on the concentration of ink as well as the diameter and number of threads of the screen. In addition, parametric settings of the printing process, such as printing speed, squeeze pressure, and distance between screen and substrate, also strongly influence the printing quality. In the present study, it is found that the reproducibility of layer thickness is quite good among the same batch of samples that are printed consecutively. In this case, the variation in the layer thickness is less than 5%. However, for samples of different batches, the thickness variation is substantially larger. Especially, when the printer is used for other tasks in between printing two batches of samples, it needs to be reset with all the employed parameters. In this case, the thickness variation can reach up to about 40% for samples of different batches. In general, one-time printing of PEDOT:PSS and P(VDF-TrFE) layers results in a thickness of about 300–500 nm and 5–7 $\mu$m, respectively. One layer of PEDOT:PSS printed on the paper substrate exhibits a sheet resistance of about 250 $\Omega\square^{-1}$.

Figure 1 shows the scanning electron microscopy (SEM) micrograph of the cross section of a sample. The printed top and bottom PEDOT:PSS electrodes (327.9 and 298.4 nm thick, respectively), the P(VDF-TrFE) layer (5.69 $\mu$m thick), and part of the paper substrate are clearly seen. Additionally, the image illustrates good bonding between adjacent layers. Figure 2 shows the surface morphology of the paper substrate (left), the P(VDF-TrFE) layer, and the top PEDOT:PSS layer (right) of a sample. The arithmetic mean roughness (Ra) values are 0.394, 0.165, and 0.139 $\mu$m for the paper substrate, the P(VDF-TrFE) layer, and the top PEDOT:PSS electrode, respectively. The printed layers have a relatively large roughness, which is mainly due to the rough surface of the paper substrate.

Depending on the molar ratio of VDF and TrFE and on the preparation conditions, P(VDF-TrFE) crystallizes into various phases, including $\beta$-phase (all-trans confirmation, TTTT), $\alpha$-phase (trans-gauche conformation, TTGT), and $\gamma$-phase (TTTG). $\beta$-phase is highly polar and ferroelectric, $\alpha$-phase is nonpolar in nature, and $\gamma$-phase lies in between. It is known that P(VDF-TrFE) crystallizes directly into $\beta$-phase when the content of VDF is within 50–80 mol\%\cite{8}. This is a big advantage over PVDF, whereas PVDF usually crystallizes into $\alpha$-phase by solution-casting or melt-cooling methods. Mechanical stretching is the most conventional procedure to convert $\alpha$-phase PVDF into $\beta$-phase, which is not easily applicable for printed film with substrate. Therefore, P(VDF-TrFE) is often employed for the preparation of printed piezoelectric polymer devices. Herein, Fourier-transform infra-red spectroscopy with attenuated total reflectance (FTIR-ATR) spectrum of the printed P(VDF-TrFE) layer (unpoled) was measured to study its phase composition (Figure 3). Different crystalline phases absorb the irradiated infrared light at certain specific frequencies. The frequency and intensity of the absorption form characteristic spectral fingerprints for the crystalline phases. According to literature\cite{23}.
the absorption bands at 510, 850, and 1288 cm\(^{-1}\) are assigned to β-phase, which are clearly seen in Figure 3. In contrast, the bands for α-phase (at 530, 614, 765, 795, and 976 cm\(^{-1}\)) are not observed. It is more complicated to identify γ-phase. Compared with β-phase, γ-phase has similar chain conformations and therefore close characteristic bands. For instance, the band at 512 cm\(^{-1}\) for γ-phase is very close to the band at 510 cm\(^{-1}\) for β-phase. However, it is believed that bands at 776, 812, 833, and 1234 cm\(^{-1}\) are exclusively assigned to γ-phase.[24] All these bands are hardly discernable in Figure 3. The FTIR-ATR spectrum of a poled sample was also measured, and no difference is observed between the spectra for unpoled and poled samples. Therefore, the FTIR-ATR spectra indicate that the printed P(VDF-TrFE) layer with or without poling contains mainly β-crystalline phase and an almost negligible amount of α- and γ-phase. In a previous study[25], it was reported that the average packing density and crystallinity of P(VDF-TrFE) films increase upon poling as revealed by thermal analysis and X-ray diffraction measurements, although the difference is not found between the vibrational spectra for samples with and without poling. Fang et al. reported that a treatment with cyclic electric field leads to higher packing density and more perfect all-trans conformation of P(VDF-TrFE) films.[26] More detailed studies regarding the influence of poling on the structure and properties of the printed P(VDF-TrFE) layer will be carried out in our future investigations.

2.2. Dielectric Spectroscopy

Figure 4a shows the frequency spectrum of the capacitance C (left ordinate) and dielectric loss factor tanδ (right ordinate) of an array sample measured before and after poling. It can be seen that the sample capacitance noticeably decreases after poling, as observed with ferroelectric P(VDF-TrFE) polymers by other authors.[27–29] With the rather low measuring electric field, the dielectric response of semicrystalline P(VDF-TrFE) originates...
mainly from the alignment of dipoles in the amorphous phase and the weak fluctuation of polar crystals. During poling, part of the amorphous phase is forced to change into the crystalline phase. Poling also leads to orientation of dipoles, removal of the gauche defects along the chains, and denser and more regular packing of the chains. All these factors render the ferroelectric polymer dielectrically less active. Additionally, the so-called self-healing events with tiny sparks often take place at the weak points during poling of the relatively large samples. These events remove the electrode locally, reducing the electroded area and hence the sample capacitance after poling.

The real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the dielectric permittivity are shown in Figure 4b. The printed P(VDF-TrFE) film shows a permittivity of 9.6 at 1 kHz, consistent with the value of $10^{-11}$ at 1 kHz as specified by the manufacturer. This indicates that printing quality of the P(VDF-TrFE) layer is satisfactory and the PEDOT:PSS electrodes work quite well at low frequencies.

It is known that P(VDF-TrFE) with metal electrodes exhibits a stable dielectric performance with a rather small drop in permittivity and low loss at least up to 1 MHz. Figure 4b shows that the permittivity of the printed array sample already decreases noticeably at 2 kHz. At about 6 kHz, the permittivity drops to half of the value at 100 Hz. This behavior originates from the series connection of the capacitive P(VDF-TrFE) layer and the resistive PEDOT:PSS electrodes, as observed on other ferroelectric films with nonmetallic electrodes. The circuit effect exhibits a typical Debye relaxation with a relaxation time of $\tau = R_C$, where $R_s$ and $C_f$ are the series resistance of the electrodes and the capacitance of the P(VDF-TrFE) layer, respectively. Therefore, the measured dielectric relaxation spectra reveal little information on the true dielectric properties of the P(VDF-TrFE) film. To study the intrinsic dielectric properties, the film should be coated with electrodes having a negligibly small resistance. The series connection of $R_s$ and $C_f$ results in a fall-off frequency of 5.6 and 8 kHz for the array sample before and after poling, respectively (Figure 4b). The relatively large resistance of the PEDOT:PSS electrodes hinders the use of the device in a high frequency range.

2.3. Poling

The P(VDF-TrFE) layer must be poled to render it piezoelectric. For characterizing the poling process, a bipolar triangular voltage consisting of two positive semicycles and two negative semicycles was applied to the sample (Figure 5a). With the printed PEDOT:PSS top and bottom electrodes, it is possible to pole the array samples with a sufficiently high electric field, even though the sample area is relatively large. Local breakdown events often take place, especially in the first voltage cycles, possibly due to local irregularities in samples such as impurities, pinholes, and non-uniform thickness. Usually, the breakdown events do not lead to destruction of the sample. Rather, they burn away the irregularities and cause evaporation of the electrodes in the surrounding regions (Figure S1, Supporting Information). The breakdown events then extinguish, and still the sample can be successfully poled. Such a self-healing effect can be attributed to the low decomposition temperature and thin thickness of the PEDOT:PSS electrodes. The decomposition temperature of PEDOT is $350^\circ C$, much lower than that of the metal electrode such as Al ($660^\circ C$). Consequently, burning away the PEDOT:PSS electrode requires much less energy and is less destructive for the sample than metal electrodes. To the best of the authors’
knowledge, the array samples reported here are the largest that have been made and poled with the straightforward contact poling method in a laboratory setting.

Also shown in Figure 5a is the current determined by measuring the voltage across a standard resistor of 987 Ω. For the first positive and negative semicycles (1 and 3, respectively), the recorded current contains three contributions as given by

\[ i = i_p + i_{cap} + i_{con} = A \frac{dP}{dt} + C \frac{dV}{dt} + \frac{V}{R} \]  

(1)

where \( A, P, C, \) and \( R \) are the area, ferroelectric polarization, capacitance, and electrical resistance of the sample, respectively, \( V \) is the voltage applied to the sample, and \( t \) is time. The first term of Equation (1) originates from the orientation of dipoles, the second from charging of the sample capacitance, and the third from the conductivity of the sample. For the second semicycles 2 and 4, only the second and the third terms are present as the molecular dipoles are already oriented in the previous semicycles. As shown in Figure 5a, the current from capacitive charging and conductivity of the sample is quite small compared with that from polarization.

Hysteresis loops are determined by integrating the first term, i.e., the current solely from the orientation of dipoles, which is attained by subtracting the current in the second semicycle from that in the first semicycle. Figure 5b shows the net current from the orientation of dipoles (right ordinate) and the corresponding polarization-versus-electric-field \( (P(E)) \) hysteresis loop (left ordinate). A remanent polarization \( (P_r) \) of 71.5 mC m \(^{-2}\) and a coercive field \( (E_C) \) of 50 MV m \(^{-1}\) are determined for the array sample. The values are in good agreement with those reported in the literature.\(^{[21]}\) Figure 5c shows \( P_r \) as a function of the amplitude of the applied electric field. A fresh sample was poled using the aforementioned bipolar voltage waveform with increasing amplitude, and \( P_r \) was determined from the hysteresis loops for each voltage amplitude. A threshold behavior is clearly shown in Figure 5c. \( P_r \) increases sharply above the coercive field and reaches saturation at about 100 MV m \(^{-1}\).

### 2.4. Acoustic Performance and Further Improvement

The sound emission of piezoelectric loudspeakers relies on the piezoelectric sensitivity of the active layer. Thanks to the inverse piezoelectric effect, the dimension of the P(VDF-TrFE) layer varies upon a driving electric field. In the case of our printed loudspeakers, the strain is given by \( x_i(t) = d_{3i}E_3(t) \), where \( d_{3i} \) \((i = 1, 2, 3)\) is the piezoelectric coefficient and \( E_3(t) \) is the driving electric field applied in the thickness direction. When the P(VDF-TrFE) layer together with the paper substrate is bent and clamped at the edges, an extensional force is generated upon application of a driving electric field \( E_3(t) \), which is given by \( F_3(t) = Y_TA_3 \varphi_3E_3(t) \), where \( Y_T \) is the Young’s modulus of the P(VDF-TrFE) layer and \( A_3 \) is the cross-sectional area of the P(VDF-TrFE) layer. \( F_3(t) \) has a nonzero component along the symmetric axis of the speaker. As a result, all the printed layers and the paper substrate are driven to vibrate as a membrane.\(^{[12]}\) In several previous studies, the generation of remarkable sound signals with bent piezoelectric polymer films was investigated.\(^{[15–17,33]}\)

It is known that the piezoelectric sensitivity of a ferroelectric film is strongly related to its remanent polarization. Figure 6a shows the output SPL of a single printed piezoelectric loudspeaker unit \((10 \times 6 \text{ cm in area})\) with different remanent polarizations. SPL is given by

\[ \text{SPL} = 20 \log \left( \frac{P_A}{P_{\text{ref}}} \right) \]  

(2)

where \( P_A \) is the root mean square (RMS) value of the sound pressure and \( P_{\text{ref}} = 20 \mu \text{Pa} \) is the reference pressure for SPLs in air. At first, acoustic measurement was carried out with a fresh loudspeaker unit \( (P_r = 0) \). Then the same loudspeaker unit was poled as described earlier with increasing voltage amplitude. For each voltage amplitude, the remanent polarization was obtained by recording the hysteresis loop, followed by an acoustic measurement in the acoustically dry environment. As shown in Figure 6a, the SPL of the fresh loudspeaker unit is about 30 dB, representing the background SPL of the measuring environment. The SPL response is enhanced a lot even if the sample is just slightly poled to a \( P_r \) of 7.8 mC m \(^{-2}\). Over a frequency range from about 1.6 to 8.7 kHz, the SPL already reaches about 50 dB \((\pm 5 \text{ dB})\). For lower frequency, the SPL clearly descends, as typically observed for
piezoelectric loudspeakers.\textsuperscript{13} At about 8.4 kHz, the SPL sharply decreases with increasing frequency, which is related to the aforementioned fall-off frequency of the sample. As \( P \) increases, the SPL is improved, especially in the medium frequency range from about 2 to 9 kHz, over which the piezoelectric loudspeakers are more effective. An increase in the SPL is observed also for a lower frequency range from 400 Hz to 2 kHz but is less pronounced. For the maximum \( P \) of 70.3 mC m\(^{-2}\), an SPL of 79 dB is obtained at a frequency of about 6 kHz. The SPL response curves display peaks and dips which might be due to the resonances of the sample and/or the measuring environment. Theoretical and experimental investigations on this behavior are under way in our group. For different \( P \), the profile of the peaks and dips slightly changes, as poling changes the mechanical properties of the P(VDF-TrFE) layer.\textsuperscript{29}

Figure 6b shows the SPL of array loudspeakers with different numbers of units (\( N \)). Up to the fall-off frequency of about 8 kHz, the frequency response profile does not change noticeably; thus, the array speakers can be considered as a single acoustic source. In this case, the absolute sound pressure \( P_a \) is proportional to the sample area. The SPL curve for two loudspeaker units exhibits an increase of about 6 dB in SPL in comparison with that for a single unit. This is to be expected due to the area of the speaker and hence \( P_a \) is doubled. SPL keeps increasing when \( N \) increases further. However, as the SPL is a logarithmic function of pressure, the increase in SPL slows down with higher \( N \).

For piezoelectric sensors and actuators, the multilayer structure is often used to enhance the performance of devices. The sensitivity and frequency response characteristics of the multilayer-structured device strongly depend on the configuration and the number of layers. Herein, multilayer samples with two loudspeakers were prepared by printing the conducting-ferroelectric-conducting polymers layer arrangements on both surfaces of the paper substrate (Figure 7a).

When the two loudspeakers work together at the same time, they can be driven in phase or out of phase. Figure 7b shows the output SPL of such a sample when the two loudspeakers are driven individually, in phase and out of phase, respectively. The two loudspeakers exhibit similar SPL responses when being driven individually. Slight differences are observed, which might be caused by small differences in the sample parameters that cannot be avoided in the laboratory. The SPL increases by about 6 dB when the two speakers are driven in phase. With a piezoelectric extensional force, the P(VDF-TrFE) layer operates as an actuator and brings all the printed layers and the paper substrate to vibrate as a membrane. The generated force from each loudspeaker is added up when the two loudspeakers are driven in phase, and therefore the overall driving force is about twice as large as that from each loudspeaker individually. The acoustic pressure of the bent piezoelectric loudspeaker is proportional to the overall driving force.\textsuperscript{15,16} As a result, the acoustic pressure is doubled and a 6 dB increase in SPL is obtained. To show a potential application in the field of smart packaging, a coffee box (Toning box, or T-Box) with amusement functionality was designed and equipped with such a double-layer piezoelectric polymer loudspeaker. A predesigned picture with the logo of the institute was printed on a paste paper, which was then pasted onto one side of the paper loudspeaker. The circuitry for driving the loudspeaker consisted of a commercially available battery, MP3 player, and amplifier. It was integrated and packed inside the box, with a switch controlled via the removal of the cover (Supplementary Movie, Supporting Information).

When the two loudspeakers are driven out of phase, the respectively generated force counteracts with each other, and consequently, the audio signal should be cancelled. As shown in Figure 7b, cancellation of the audio signal is observed over the whole audio frequency range. The SPL is still well above the noise floor when two speakers are driven out of phase, which is attributed to the aforementioned imperfect reproducibility of the P(VDF-TrFE) films. Slight differences between the two loudspeakers are very difficult to avoid in the laboratory, and hence a complete cancellation of the audio signal is not expected.

3. Conclusions

Piezoelectric polymer loudspeakers fully printed on paper substrates were fabricated with PEDOT:PSS as top and bottom electrodes and P(VDF-TrFE) as the piezoelectric layer in between. Loudspeaker units with an area of 10 × 6 cm\(^2\) and arrays consisting of up to five units were prepared. Dielectric spectroscopy shows a fall-off frequency of about 8 kHz for the printed loudspeaker samples, originating from the series connection of the not perfectly conducting PEDOT:PSS electrodes and the capacitive P(VDF-TrFE) layer. Therefore, the printed piezoelectric device is not suitable for applications above the fall-off frequency. Nevertheless, PEDOT:PSS electrodes are favorable for poling of the P(VDF-TrFE) layer because the self-healing process during poling is mostly nondestructive. Hysteresis loop indicates a remnant polarization \( P_r \) of about 71.5 mC m\(^{-2}\) and a coercive field \( E_c \) of 50 MV m\(^{-1}\) for the printed P(VDF-TrFE) layer. It is found
that the SPL of the fully printed piezoelectric polymer loudspeaker increases with increasing \( P \) and number of loudspeaker units. An SPL of about 91 dB is obtained with loudspeaker arrays of five units. With samples consisting of two loudspeaker arrays printed on both surfaces of the paper substrates, a further increase of 6 dB in SPL is achieved when the two loudspeakers are driven in phase. The all-printed piezoelectric polymer loudspeakers can be used for thin and highly flexible acoustic systems such as speaking books and posters as well as smart packaging.

4. Experimental Section

Sample Preparation: The fully printed loudspeakers consisted of a paper substrate, a bottom electrode, a piezoelectric polymer layer, and a top electrode. Paper sheets produced by UPM (tradename: Maxigloss) with a grammage of 90 g m\(^{-2}\) and a thickness of 67 \( \mu \)m were employed as substrates. The bottom electrode, the piezoelectric polymer layer, and the top electrode were printed in sequence through screen printing by means of a semi-aumatomatic screen printer EKRA X1-5L. The bottom and top electrodes were made of a water-based PEDOT:PSS ink (SV4, Heraeus Clevios GmbH). Prior to printing, PEDOT:PSS ink was mechanically stirred for about 10 min to enhance the dispersion of the conductive polymer. P(VDF-TrFE) (75:25 mol\%) (Arkema) was employed as the piezoelectric layer. It can be dissolved in a number of organic solvents such as methyl ethyl ketone (MEK), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), and cyclopentanone or a mixture of solvents. After the printing of each layer, a thermal treatment of 5 min at 130 °C (for PEDOT:PSS) or 10 min at 135 °C (for P(VDF-TrFE)) was implemented in an oven with ventilation.

Figure S2a, Supporting Information, schematically shows the geometry of the loudspeakers printed on paper. The bottom PEDOT:PSS electrode and the P(VDF-TrFE) layer had an area of 34 \( \times \) 11 cm\(^2\) and 34.5 \( \times \) 11 cm\(^2\), respectively. The top PEDOT:PSS electrode consisted of five parallel rectangular pieces (11 \( \times \) 6 cm\(^2\) in area each) with a separation of 9 mm between adjacent pieces. Therefore, one array contained five printed piezoelectric loudspeaker units. To avoid short-circuit connection between the top and bottom electrodes, the three printed layers were shifted such that each loudspeaker unit had a piezoelectrically active area of 10 \( \times \) 6 cm\(^2\) (the overlapping area of the top and bottom electrodes). The preparation of such array-structured piezoelectric loudspeakers was easily transferred to an inline roll-to-roll mass printing equipment. The separation between adjacent speaker units allowed cutting of the sample without the risk of short circuiting the top and bottom electrodes. However, optimization of the array structure was not intended herein.

The thickness of the printed PEDOT:PSS layers was measured by means of a 3D laser scanning microscope (VK9710, Keyence). To determine the thickness of the P(VDF-TrFE) layer, its weight was measured using an electronic balance. The thickness was calculated by \( h = W/\rho A \), where \( W \) is the weight, \( A \) is the area, and \( \rho = 1.88 \text{ g cm}^{-3} \) is the density given by the supplier.

Scanning Electron Microscopy: SEM images were taken with an FEI Nova NanoSEM 200 SEM. The sample was prepared by fracturing a printed piezoelectric polymer loudspeaker in liquid nitrogen, and the cross section was then coated with platinum electrode via plasma evaporation.

Surface Morphology: Surface morphology images and their arithmetic roughness (Ra) were also analyzed by means of the 3D laser scanning microscope (VK9710, Keyence).

Fourier-Transform Infra-Red Spectroscopy with Attenuated Total Reflectance: FTIR-ATR spectra were taken with a spectrometer (Bruker Optics, Model Alpha). For unpoled samples, the upper surface of the printed P(VDF-TrFE) layer without the top PEDOT:PSS electrode was measured. For comparison, a sample poled with an electric field of about 100 MV m\(^{-1}\) was also measured. Prior to the FTIR-ATR measurement, the top PEDOT:PSS electrode was removed by dipping the poled sample into a solution of KMnO\(_4\) + H\(_2\)SO\(_4\) + deionized (DI) water (ratio: 15 g:200 mL:1 L). The top PEDOT:PSS layer was removed within about 10 s. To remove possible MnO\(_2\) residuals on the surface, the sample was then treated shortly in a solution of Na\(_2\)SO\(_4\) + H\(_2\)SO\(_4\) + DI water (ratio: 3 g:25 mL:1 L). Finally, the sample was rinsed with DI water and dried in lab conditions.

Dielectric Spectroscopy: Dielectric spectra of the printed samples were measured with an LCR meter (E4980A, Agilent) over a frequency range from 20 Hz to 2 MHz.

Hysteresis Measurements: A hysteresis circuit as schematically shown in Figure S3, Supporting Information, was set up to study the poling behavior of the printed piezoelectric P(VDF-TrFE) layers. Samples were connected in series with a high-voltage (HV) supply (Model 5/80-HS, Trek), which was controlled by means of a function generator (TGA1244, Telemeter Electronic GmbH) and an HV resistor of 987 \( \Omega \). The current flowing through the circuit was determined by measuring the voltage of the resistor using an oscilloscope (DSO-X 2004A, Agilent) via a 100:1 probe (10076B, Agilent). A bipolar voltage sweep was applied, which allowed the separation of dipole switching from capacitive charging and conduction process. \(^{[13,36]}\)

Acoustic Measurements: Acoustic measurements were conducted in a dry environment with an RT60\(_{[500 \text{ Hz}, \ 1 \text{ kHz}]}\) of 29.8 ms evaluated using the Integrated Impulse response method in accordance with the ISO 3328 standard. Measurements were carried out with a sinus-apollo acoustic analysis system consisting of a power amplifier (PA-1122 Power Amplifier, Monacor), a microphone (M370, Microtech Gefell GmbH), and its acoustic analyzer (Sinus 315 Apollo GmbH, Leipzig), controlled with a Samurei software. The samples were clamped at both sides of the substrate along the width of each loudspeaker unit and bent into an arc with a center angle of 90° (Figure S2b, Supporting Information). The microphone was placed above the geometric center of the speaker with a distance of 1 m. The loudspeakers were driven with a sine sweep voltage of 50 Vpp and a linear sweep from 20 Hz to 20 kHz within 30 s.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

loudspeakers, multilayer structures, papers, PEDOT:PSS, P(VDF-TrFE), screen printing

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