

Turning Polymer Foams or Polymer-Film Systems into Ferroelectrets: Dielectric Barrier Discharges in Voids

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ABSTRACT

Polymer foams and void-containing polymer-film systems with internally charged voids combine large piezoelectricity with mechanical flexibility and elastic compliance. This new class of soft materials (often called ferro- or piezoelectrets) has attracted considerable attention from science and industry. It has been found that the voids can be internally charged by means of dielectric barrier discharges (DBDs) under high electric fields. The charged voids can be considered as man-made macroscopic dipoles. Depending on the ferroelectret structure and the pressure of the internal gas, the voids may be highly compressible. Consequently, very large dipole-moment changes can be induced by mechanical or electrical stresses, leading to large piezoelectricity. DBD charging of the voids is a critical process for rendering polymer foams piezoelectric. Thus a comprehensive exploration of DBD charging is essential for the understanding and the optimization of piezoelectricity in ferroelectrets. Recent studies show that DBDs in the voids are triggered when the internal electric field reaches a threshold value according to Townsend's model of Paschen breakdown. During the DBDs, charges of opposite polarity are generated and trapped at the top and bottom internal surfaces of the gas-filled voids, respectively. The deposited charges induce an electric field opposite to the externally applied one and thus extinguish the DBDs. Back discharges may eventually be triggered when the external voltage is reduced or turned off. In order to optimize the efficiency of DBD charging, the geometry (in particular the height) of the voids, the type of gas and its pressure inside the voids are essential factors to be considered and to be optimized. In addition, the influence of the plasma treatment on the internal void surfaces during the DBDs should be taken into consideration.

Index Terms — Ferroelectret, piezoelectret, dielectric barrier discharge (DBD), effective polarization, man-made dipole.

1 INTRODUCTION

CELLULAR polymers (polymer foams) were first produced during the 1960s [1]. They are now widely used for thermal insulation, shock and sound absorption, packaging, etc. Over the past 15 years, a considerable number of cellular or void-containing polymer-electret systems with significant piezoelectricity have been identified and developed. This novel class of polymer materials not only presents new challenges and chances for materials and device engineering, but also represents a new paradigm of piezo-, pyro- and ferroelectricity in soft matter. The new electroactive materials

have been named ferroelectrets. They attract considerable attention in fundamental research and are considered or employed for applications in e.g. ultrasonic receivers and transmitters, microphones and microphone arrays, curved or flat loudspeakers, electromechanical sensors and actuators, etc. For details of the history and of the recent development in this field, the reader may consult relevant review papers and the original literature cited therein [2-6].

The microscopic origin of piezo-, pyro- and ferroelectricity in ferroelectrets is significantly different from that of polar polymer ferroelectrics containing intrinsic dipoles. In order to render polymer foams piezoelectric, the voids must be internally charged under high electric fields. The charging process in ferroelectrets requires dielectric barrier discharges

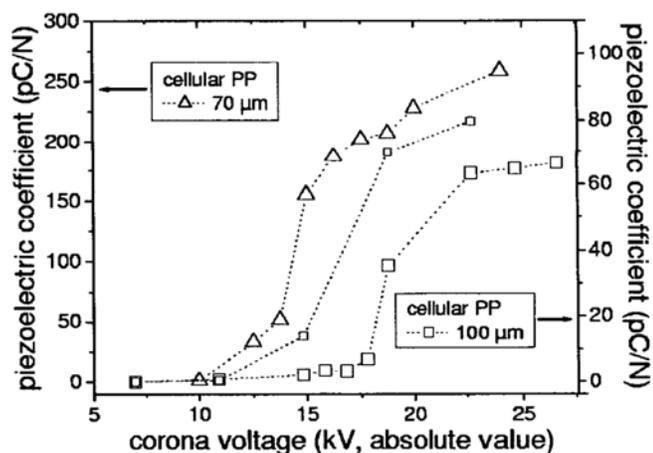


Figure 1. Piezoelectric d_{33} coefficient as a function of corona-charging voltage for positively charged 70 μm thick (triangles) cellular PP as well as for positively (larger symbols) or negatively (smaller symbols) charged 100 μm thick (squares) cellular PP [9].

(DBDs). In DBDs, at least one side of the discharge gap is insulated from the electrodes by a dielectric layer [7]. It is found that charges of opposite polarity are separated during charging and then trapped, respectively, at the internal top and bottom surfaces of the voids. Each charged void can thus be considered as a man-made macroscopic dipole, whose direction can be reversed by sufficiently high electric fields [8]. The macroscopic dipoles can be easily deformed under mechanical and electrical stresses, resulting in very large direct and inverse piezoelectricity, respectively. Depending on the material structures and the charging conditions, ferroelectrets often show piezoelectric d_{33} coefficients of hundreds of pC/N.

It has become evident that a comprehensive exploration of DBD charging is critical for understanding and optimizing the piezoelectricity of ferroelectrets. In recent years, the knowledge about the charging process in ferroelectrets has significantly advanced. Here, a brief overview on DBD charging of ferro- and piezoelectrets is provided, and recent results concerning the light emission from the DBDs in ferroelectret systems are reported and discussed.

2 THRESHOLD BEHAVIOR AND MODEL OF THE INTERNAL ELECTRICAL BREAKDOWN

The voltage dependence of the DBD charging process and the resulting piezoelectric d_{33} coefficient in ferroelectrets shows a threshold behavior as clearly seen in Figure 1, where the d_{33} coefficients of cellular-polypropylene (PP) ferroelectrets with different thicknesses are plotted as a function of the corona-charging voltage [9]. In corona charging, the internal electric field in the voids is controlled by the surface potential of the sample. The d_{33} coefficients remain nearly zero for corona voltages below the threshold. For positively charged 70 μm thick cellular PP, a threshold voltage above 10 kV is observed. For positively and negatively charged 100 μm thick cellular PP, the threshold corona voltages are above +17.5 and below -11 kV,

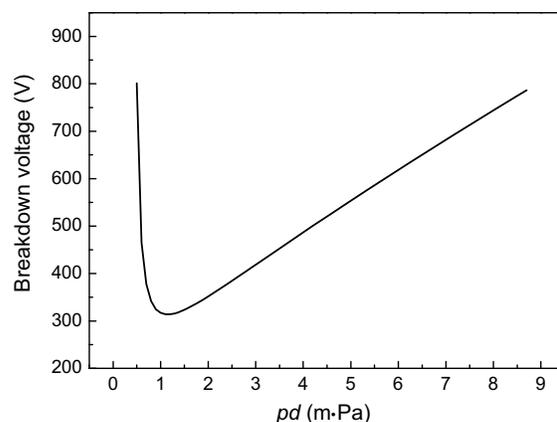


Figure 2. Paschen breakdown voltage of air as a function of the product pd .

respectively. The d_{33} coefficients increase dramatically with increasing corona voltage above the threshold. The threshold behavior is also confirmed in direct-contact charging experiments on the same types of cellular PP [10]. In direct-contact charging, the internal electric field in the voids is induced directly by the external voltage applied to the sample electrodes that had been deposited by vacuum evaporation prior to charging. For direct-contact charging, threshold voltages of -6 and -6.5 kV are observed on 70 and 100 μm thick cellular PP films, respectively.

The threshold behavior can be explained with Paschen's law which describes the breakdown voltage between parallel plates in a gas as a function of pressure and gap height. According to Townsend's model, the critical breakdown voltage of common gases in a uniform electric field is a function of both gas pressure p and electrode spacing d (which is equal to the void height in the present context) [11]

$$V = \frac{Apd}{B + \ln(pd)} \quad (1)$$

where V is the breakdown voltage in Volt, p is the pressure in Pascal, and d is the gap height in m. The parameter B is given by

$$B = \ln\left(\frac{C}{\ln(1+1/\gamma)}\right) \quad (2)$$

The constants A and C depend on the composition of the gas. For air, the values $A = 273.8 \text{ Vm}^{-1}\text{Pa}^{-1}$ and $C = 11 \text{ m}^{-1}\text{Pa}^{-1}$ are experimentally determined. $\gamma = 0.01$ is the so-called second ionization coefficient. Figure 2 shows the breakdown voltage in air as a function of the product pd . The Paschen breakdown voltage must be reached in the voids in order to ignite dielectric barrier discharges. Consequently, there exists a threshold charging voltage for inducing piezoelectricity in polymer foams. The effective charging field at the threshold is an analogue to the coercive field in ferroelectric materials. However, the mechanism for polarization is quite different: The polarization in ferroelectrics relies on the orientation of intrinsic dipoles, while the polarization in ferroelectrets requires charge separation during the DBDs and charge trapping on the internal surfaces of the voids.

The charging process was theoretically analyzed with a simplified model for the piezoelectricity of ferroelectrets [12, 13]. The model consists of n layers of polymer separated by $(n-1)$ layers of gas [14, 15]. The relative dielectric constants, thicknesses and the electric fields of the polymer and the gas layers are ϵ_{pr} , d_{pi} , E_{pi} and ϵ_{gr} , d_{gi} , E_{gi} , respectively. The equivalent charge densities at the interfaces of gas and polymer are $\pm\sigma_i$, while σ_0 and $-\sigma_0$ are the charge densities induced on the electrodes. For simplicity, the thickness of each gas layer as well as the charges trapped at the gas/polymer interfaces are assumed not to vary across the sample ($d_{g1} = d_{g2} = \dots = d_{g(n-1)}$ and $\sigma_1 = \sigma_2 = \dots = \sigma_n$). The piezoelectric d_{33} coefficient calculated from such a simplified model is given by [14]

$$d_{33} = \frac{\epsilon_{gr}\epsilon_{pr}d}{Y} \frac{d_p \sum d_{gi}\sigma_i}{d_g(\epsilon_{gr}d_p + \epsilon_{pr}d_g)^2}. \quad (3)$$

When an external voltage V is applied, the electric field in the i^{th} gas layer is given by [15]

$$E_{gi} = \frac{\epsilon_0\epsilon_{pr}V - \sigma_i d_p}{\epsilon_0\epsilon_{gr}d_p + \epsilon_0\epsilon_{pr}d_g}, \quad (4)$$

where $d_p = \sum_{i=1}^n d_{pi}$ and $d_g = \sum_{i=1}^{n-1} d_{gi}$ are the total thicknesses of all the polymer layers and all the gas layers, respectively.

We consider the case where a linearly increasing voltage V is applied to a fresh sample [12, 13]. Initially, $\sigma_i = 0$ when E_{gi} is lower than the threshold for Paschen breakdown E_{th} . E_{gi} increases with increasing V , and Paschen breakdown is ignited when the field becomes higher than E_{th} , leading to a non-zero σ_i . The voltage corresponding to E_{th} is

$$V_{th} = E_{th} \left(\frac{\epsilon_{gr}}{\epsilon_{pr}} d_p + d_g \right). \quad (5)$$

During Paschen breakdown inside the voids, separated charges of opposite polarity are trapped on the internal top and bottom surfaces of the voids, respectively. The trapped charges partly compensate the applied electric field, and the breakdown is extinguished when E_{gi} decreases back to E_{th} , which is known as choking effect in conventional DBDs. When V is further increased, however, the breakdown process continues and σ_i increases continuously until the extinguishing condition $E_{gi} = E_{th}$ is again met. At this point, σ_i is still determined by Equation (4). Substitution into Equation (3) yields the piezoelectric coefficient

$$d_{33} = \frac{\epsilon_{gr}\epsilon_{pr}d}{Y} \frac{\epsilon_0\epsilon_{pr}(V - V_{th})}{(\epsilon_{gr}d_p + \epsilon_{pr}d_g)^2} \quad (6)$$

If the electric field generated by the trapped charges is higher than E_{th} , it is obvious that DBDs in the opposite direction (back discharges) will be triggered when the external voltage is turned off. The minimum voltage required for the occurrence of back discharges is

$$V = 2E_{th} \left(\frac{\epsilon_{gr}}{\epsilon_{pr}} d_p + d_g \right) = 2V_{th} \quad (7)$$

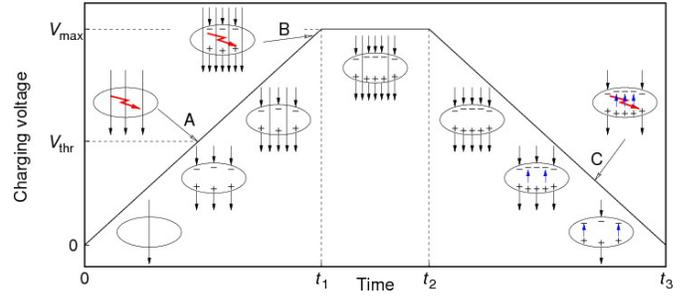


Figure 3. Schematic view of the DBD charging process in a single polymer void. When the charging voltage reaches the threshold value V_{th} , Paschen breakdown is ignited (A). At higher voltages, a second discharge may occur (B). During ramping down the voltage, the reverse electric field from the trapped space charges may lead to back discharges (C) [17].

Again, the back discharges are extinguished when $E_{gi} = E_{th}$. Note that E_{gi} now has opposite sign and direction as the previous E_{gi} under the externally applied voltage. Thus, E_{th} determines the maximum value of σ_i that can be attained after charging with a given external voltage V . From these considerations, the piezoelectric d_{33} coefficient to be found in ferroelectrets after charging is described by

$$d_{33} = \begin{cases} 0, & (V < V_{th}) \\ k(V - V_{th}), & (V_{th} \leq V \leq 2V_{th}) \\ kV_{th}, & (V > 2V_{th}) \end{cases} \quad (8)$$

where the factor k is given by

$$k = \frac{\epsilon_0\epsilon_{gr}\epsilon_{pr}^2 d}{Y(\epsilon_{gr}d_p + \epsilon_{pr}d_g)^2} \quad (9)$$

As can be seen from Equation (8), the d_{33} coefficient of ferroelectrets remains zero when the charging voltage V is lower than the threshold value V_{th} . For voltages above the threshold, d_{33} increases linearly with V until the latter reaches $2V_{th}$. For charging voltages V higher than $2V_{th}$, the d_{33} coefficient does not increase anymore. It always assumes the constant saturation value. Our experimental results show

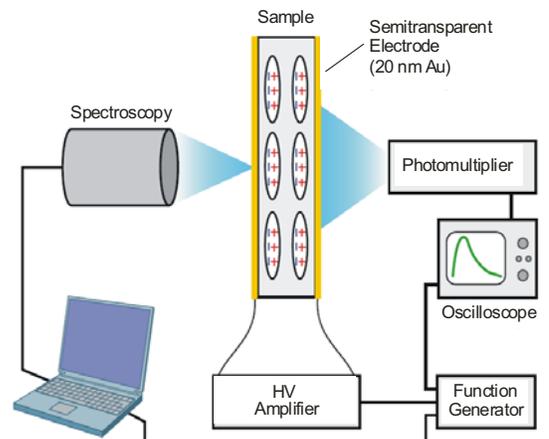


Figure 4. Schematic setup for a spectroscopic analysis of the dielectric barrier discharges (DBDs) in the voids of ferroelectrets [20, 21].

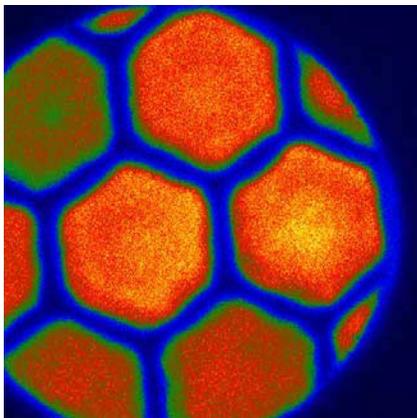


Figure 5. Color-coded EM-CCD image of a polycarbonate ferroelectret system with hexagonal voids under a positive sinusoidal voltage (frequency of 100 Hz and peak-to-peak value V_{pp} of 3 kV). The EM-CCD camera is internally triggered with an exposure time of 5 s [22].

reasonable agreement with the theoretical analysis, while a small deviation is attributed to the wide distribution of void sizes and shapes [12]. Zhukov and von Seggern suggested a similar analysis for layered fluoropolymer ferroelectrets (FEP-ePTFE-FEP sandwiches) [16].

More recently, a schematic model for the DBD charging process in ferroelectrets has been proposed, as shown in Figure 3 [17]. Internal breakdown (Paschen breakdown) in the voids is initiated when the voltage reaches the required threshold value (in this sense, the electric field in the voids is comparable with the “coercive field” in ferroelectrics). Charges of opposite polarity are separated during the DBDs and are subsequently trapped on the top and bottom surfaces of the voids, respectively (point A in Figure 3). The trapped charges induce an electric field opposite to the externally applied field and thus eventually extinguish the discharge. As the applied voltage increases further, a second series of breakdown events may occur, and the density of the internally trapped charges strongly increases (point B in Figure 3). When the applied voltage is reduced, the electric field of the trapped charges may overcompensate the applied field and may thus be able to trigger back discharges ((point C in Figure 3)).

3 LIGHT EMISSION FROM THE DIELECTRIC BARRIER DISCHARGES

The DBDs in ferroelectrets are always accompanied by light emission that can be easily photographed [9, 18]. The light emission originates from electronically excited and/or ionized gas molecules inside the voids and can be used as a diagnostic tool for characterizing the DBDs [17, 19]. The setup used for the spectroscopic analysis of the DBDs in ferroelectrets is schematically shown in Figure 4 [20, 21]. The sample, metalized on both sides with semitransparent gold electrodes (diameter of 16 mm and thickness of 20 nm), is mounted in a light-tight chamber. High voltages with suitable waveforms are applied directly to the sample electrodes by means of a high-voltage amplifier controlled by a function generator.

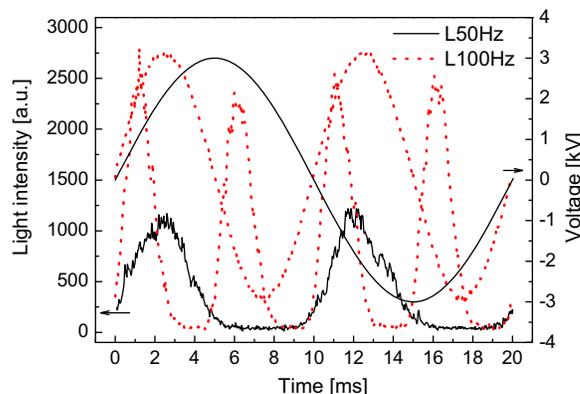


Figure 6. Transient light emission from a cellular PP ferroelectret under sinusoidal voltages at two different frequencies (black and red curves).

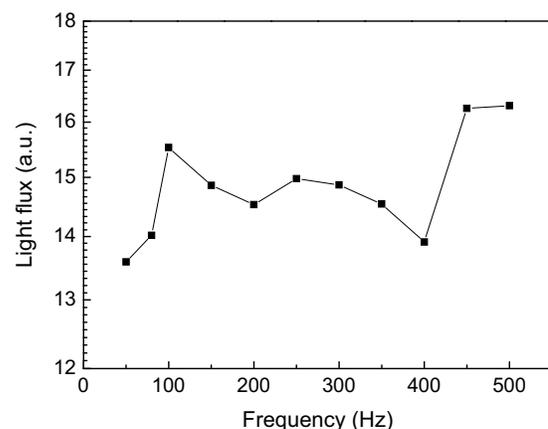


Figure 7. Light flux for one cycle of the sinusoidal voltage as a function of frequency.

The light emission is synchronously measured by a photomultiplier tube (PMT) from one side of the sample and by a spectroscopic system from the other side. The spectroscopic system consists of an optical fiber, a grating monochromator, and a PC-controlled electron-multiplying charge-coupled device (EM-CCD) camera. Spatially resolved images of the samples during charging are taken by the EM-CCD camera connected to the chamber via a lens. In order to suppress light emission from corona discharges at the periphery of the electrodes, either the edges of the electrodes are covered with silicon rubber, or the electrode areas of the sample are covered by a plastic mask with a central circular opening (open diameter of 8.5 mm).

Figure 5 shows the spatially resolved light emission from a void-containing polycarbonate ferroelectret system under a positively biased sinusoidal voltage with a peak-to-peak amplitude V_{pp} of 3 kV and a frequency of 100 Hz [22]. The sample is fabricated by sticking two polycarbonate films to a grid produced from double-sided adhesive tape by means of computer-controlled laser cutting. The hexagonal openings of the grid structure lead to honeycomb-shaped voids inside the three-layer system, which can be internally charged by DBDs under high voltages. In Figure 5, the hexagonal structure is clearly seen. The difference between the light intensities of individual voids is attributed to small differences in the void geometries which cannot be avoided with samples that are prepared individually in the laboratory.

The time-dependent light emission from a cellular PP sample under a sinusoidal voltage with a peak-to-peak amplitude $V_{pp} = 6$ kV and frequencies of 50 or 100 Hz is shown in Figure 6. Two light-emission peaks are observed for each voltage cycle regardless of the frequency. As can be seen from the figure, light emission starts shortly before the voltage changes sign because of the choking effect in the DBDs. Experimental results show that the repeated light emission is not influenced by an additional dc offset bias voltage superimposed onto the sinusoidal voltage waveforms. This is reasonable, since DBDs are extinguished very quickly by the choking effect under dc voltages, and repeated DBDs are controlled only by the voltage variations, i.e. by the sinusoidal components in this case. The total light flux can be obtained by integrating the light intensity over time. The total light flux during one cycle of the sinusoidal voltage is plotted in Figure 7 as a function of frequency. No obvious dependence on the frequency of the time-dependent voltage is observed for the light flux per cycle, which is expected, since always the same number of practically identical DBDs is generated during each cycle. For the same reason, the power of conventional DBDs in a given configuration and under a fixed peak voltage is directly proportional to the frequency [7].

Analysis of the optical emission spectrum (OES) is an effective method for diagnosing DBDs [23-26]. The OES of the DBDs in cellular PP ferroelectrets under positively biased sinusoidal voltages $V = \frac{1}{2}V_{pp} [1 + \sin(2\pi ft)]$ with a frequency of 100 Hz and different V_{pp} values has been recorded within the near-UV and visible spectral range. There is no detectable OES when V_{pp} is lower than 3 kV, which is in agreement with the PMT results [17]. Above 3 kV, an OES can be clearly detected. Part of the spectrum for a peak-to-peak voltage V_{pp} of 6 kV is shown in Figure 8 [19]. The spectrum shows strong emission from the second positive system (SPS) of molecular nitrogen, $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$, and from the first negative system (FNS) of N_2^+ , $N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_g^+)$, consistent with a DBD in air.

The appearance of the FNS of N_2^+ directly confirms the ionization of molecular nitrogen during the DBDs. The V_{pp}

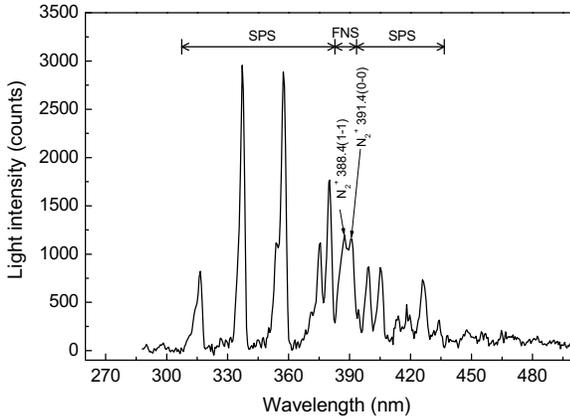


Figure 8. Optical emission spectrum of a cellular PP ferroelectret under a positive sinusoidal voltage (frequency of 100 Hz and V_{pp} of 6 kV). The EM-CCD camera is internally triggered with an exposure time of 4 s. [19]

dependence of the intensity of the spectral bands, e.g. the N_2 SPS ($0 \rightarrow 0$) and N_2^+ FNS ($0 \rightarrow 0$) bands (located at 337.1 and 391.4 nm, respectively) shows the same trend as the charging-voltage dependence of the piezoelectric d_{33} coefficient [17]. Therefore, light emission from the DBDs in ferroelectrets is strongly correlated with their piezoelectricity. In addition, the band strength ratios in the spectrum provide information on the electric field inside the DBDs [27]. From a spectroscopic analysis, the electric field during the DBDs in cellular PP ferroelectrets is found to be between 21 and 28 MV/m. The values are in good agreement with the breakdown strength in air for voids with heights between 10 and 15 μm , as predicted by the Townsend breakdown model.

4 ACOUSTICAL AND PIEZOELECTRICAL RESPONSE OF THE POLARIZATION

The build-up of the effective polarization in ferroelectrets under suitable voltage waveforms has been studied by means of acoustical measurements in combination with dielectric resonance spectroscopy [28]. In order to generate a sound signal, a sinusoidal voltage with a frequency of 1 kHz and a peak-to-peak voltage V_{pp} of 100 V is applied to cellular PP foams. An additional dc bias voltage is superimposed onto the sinusoidal voltage, and the sound signal emitted from the sample is measured with a microphone. Under laboratory conditions, the amplitude of the sound signal emitted from the sample is proportional to the absolute value of d_{33} . According to the common model for ferroelectrets, the d_{33} coefficient under a dc bias voltage is given by [15]

$$d_{33} = \frac{d}{Y} \frac{\epsilon_{pr} d_1 \sigma_{eff} - \epsilon_0 \epsilon_{pr}^2 V_{bias}}{(d_1 + \epsilon_{pr} d_2)^2} \quad (10)$$

where V_{bias} is the external voltage applied to the electrodes, and $\sigma_{eff} = \sum d_{2i} \sigma_i / \sum d_{2i}$ is the effective charge density on the polymer/air interfaces on both sides of a single air gap. According to equation (10), the sound signal radiated from the sample under a dc bias voltage has contributions not only from the effective charge density (the first term in the equation), but also from the Maxwell stress (the second term in the equation). At low bias voltage V_{bias} , the piezoelectricity of ferroelectrets is proportional to the external voltage [29], since σ_{eff} can be considered constant at a dc bias voltage well below the threshold for DBD inception.

However, when the dc bias voltage is higher than the threshold voltage, DBDs are triggered in the voids, which in turn change the effective charge density σ_{eff} . Therefore, a “butterfly” curve is obtained for the microphone signal under linearly increasing and then decreasing dc bias voltages if their maximum value exceeds the threshold (Figure 9a).

The absolute values of the piezoelectric d_{33} coefficients under zero-charging-field have been obtained by means of dielectric resonance spectroscopy (DRS) immediately after the voltage cycles with an external dc bias. Young’s modulus and d_{33} were determined by fitting the real part of the measured capacitance (inset of Figure 9b) to the relevant theoretical formula [30, 31]. By comparing the microphone signals

without a charging field with the absolute d_{33} values determined by means of DRS immediately after charging, the microphone-signal measurements could be calibrated and converted into piezoelectric d_{33} coefficients. The quantities d_1 and d_2 are determined from the density of the samples and from the measured sample thicknesses, since the density of solid PP is known and the density of air can be approximated as zero. A polarization-voltage (P - V) hysteresis loop is obtained by evaluating the data according to equation (10). Figure 9b shows the build-up of the effective polarization in a cellular PP ferroelectret as a function of the applied dc-bias voltage. Its features are similar to those typically found in hysteresis curves of ferroelectrics. From the figure, the threshold voltage and the remanence of the effective polarization can be determined. It should be noted that a significant reduction of σ_{eff} is observed when the dc bias voltage decreases from its maximum to zero, which is due to back discharges. The back discharges originate from the over-compensation of the external electric field from the bias voltage V_{bias} by the internal field of the space charges trapped

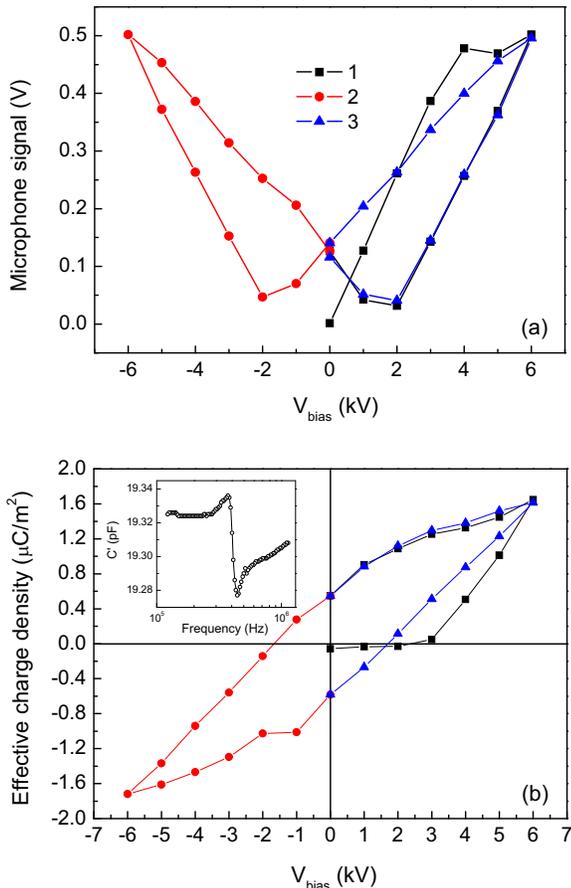


Figure 9. (a) Microphone signal as a function of the bias voltage V_{bias} applied to the sample electrodes. The maximum absolute voltage is 6 kV. A fresh, uncharged sample with a thickness of 72 μm was used for the positive half cycle (curve 1), followed by a negative half cycle (curve 2) and subsequently a second positive half cycle (curve 3). (b) Effective charge density σ_{eff} (calculated from the experimental data shown in (a) as a function of V_{bias}). The inset shows the dielectric resonance spectrum from which the absolute d_{33} coefficient corresponding to the zero-field microphone signal was calculated [28].

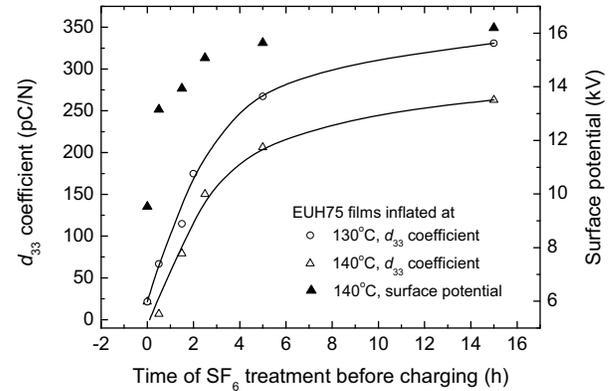


Figure 10. Pre-inflated EUH75 cellular PP film: Surface potential and piezoelectric d_{33} coefficient after charging as a function of the SF_6 treatment time before charging. The lines are guides for the eye only [33].

at the top and bottom surfaces of the voids [17]. The experimental results indicate that suppressing the back discharges could provide a pathway to a significantly enhanced piezoelectricity.

5 INFLUENCE OF GAS TYPE AND GAS PRESSURE ON THE CHARGING PROCESS

As already mentioned, the macroscopic dipoles in ferroelectrets are produced by means of the DBDs inside the voids. Therefore, the gas compositions inside the voids as well as the gas pressures have significant influence on the charging process. In corona discharges used for electret charging, the ambient gas environment also plays a crucial role, since it determines the maximum corona voltage that can be applied and the maximum surface potential that can be obtained. Paajanen *et al.* studied the effect of gas compositions on the corona charging of cellular PP foams in different gases at elevated pressures [32]. It was found that higher corona voltages can be employed with various gases of higher electrical breakdown strength, which results in more efficient charge separation inside the voids and thus also higher piezoelectricity. Especially, piezoelectric d_{33} coefficients of up to 790 pC/N were obtained when the voids of the sample had been filled with N_2 gas under high pressure. This d_{33} value is more than four times that of samples charged under standard laboratory conditions. The large enhancement was attributed to the higher dielectric strength of N_2 and to its lower moisture content compared to atmospheric air.

In reference [32], it was reported that large SF_6 molecules were not able to penetrate into the voids of the 70 μm thick cellular PP foams used in the experiments. However, the penetration of SF_6 into the sample as well as the beneficial effect on the charging efficiency during DBDs depends on the microscopic void structure of the respective samples [33]. For cellular PP foams with larger void dimensions and a low Young's modulus of around 1 MPa, the penetration of SF_6 into the cellular voids is possible after a long-term pressure treatment, as confirmed by *in-situ* thickness measurements. Figure 10 shows the piezoelectric d_{33} coefficient as a function

of the treatment time in SF₆. The d_{33} coefficient increases with increasing treatment time. An improvement by a factor of up to 1.5 is achieved for a treatment time of 15 h. For cellular PP foams with smaller void sizes and a higher Young's modulus of about 5.8 MPa, the sample thickness keeps decreasing with increasing treatment time, which indicates that the large SF₆ molecules are not able to penetrate into the voids, whereas the air molecules leak out of the voids under the high pressure. However, a much higher corona voltage up to -60 kV can be applied in an SF₆ atmosphere, leading to much higher surface potentials. Consequently, the voids can also be charged to higher levels, and an enhancement factor of 4 and 3 for the d_{33} coefficient is achieved after short and long treatment times, respectively. In order to exploit the beneficial effects of charging in SF₆ gas, only short treatment times are necessary for stiffer polymer foams with smaller void sizes (where only the level of surface charging is directly enhanced), whereas for softer foams with larger void sizes, longer treatment times are required in order to fill the voids with SF₆ molecules.

According to Paschen's law, the breakdown voltage at a given void height can be modulated through a pressure change inside the void. The capacitance of the sample is measured as a way to monitor the thickness change [34]. For pre-inflated cellular PP foams (trade name PQ50), a sudden drop (or a sudden increase) of the capacitance is observed when samples are subjected to vacuum (or to high pressure, respectively). The observation indicates thickness changes of the samples caused by the difference between the ambient pressure and that inside the voids. However, the capacitance of the sample recovers to approximately its initial value after sufficient time (typically several hours) has elapsed, which indicates that the internal and external pressures equalize as a result of gas diffusion. If the sample morphology is analyzed on a cross section we find that most of the voids have a height lower than 6 μm . At standard atmospheric pressure of 101 kPa, the Paschen breakdown voltage has its minimum at a height of around 8 μm (cf. Figure 2). Therefore, an increase of the internal pressure lowers the breakdown voltage for voids with heights lower than 8 μm . Unfortunately, the chargeability of

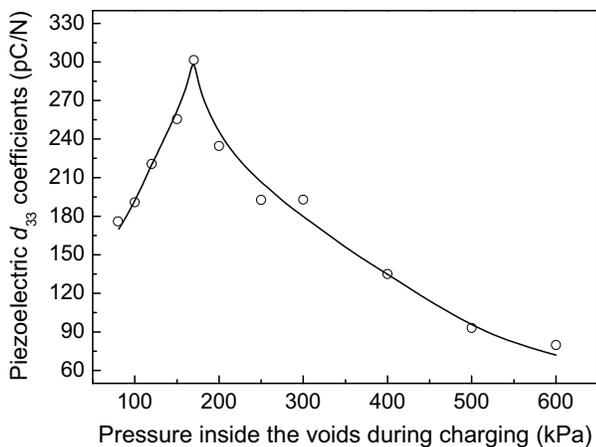


Figure 11. Piezoelectric d_{33} coefficient as a function of pressure inside the voids during charging (open circles). The line is a guide for the eye only [35].

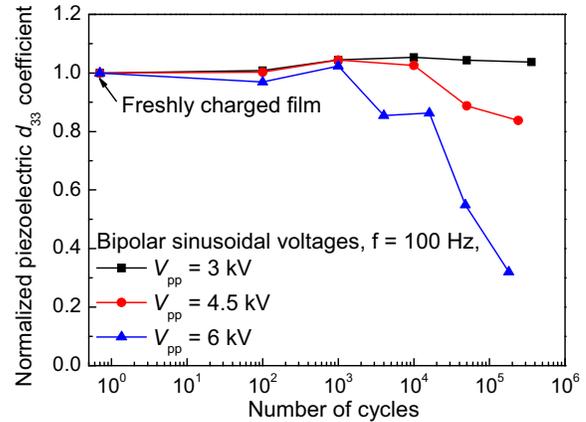


Figure 12. Normalized piezoelectric d_{33} coefficient as a function of the logarithm of the number of cycles (N). Fatigue was observed under a bipolar sinusoidal voltage with a frequency of 100 Hz and an amplitude as indicated. Cycle numbers below 10⁰ indicate freshly charged films [38].

the voids with a height larger than 8 μm is reduced at the same time. Thus, the trade-off between the two effects must be considered. For the above-mentioned cellular PP sample, optimal piezoelectricity is achieved by charging at a pressure around 170 kPa (Figure 11) [35].

6 FATIGUE UNDER REPEATED DIELECTRIC-BARRIER DISCHARGES

In the polymer industry, non-thermal plasmas found in low-pressure glow discharges as well as in high-pressure (atmospheric) corona discharges and DBDs are often used to modify the surface properties of polymers [7, 36, 37]. DBDs produce a variety of species including energetic and reactive monatomic and diatomic charged gas particles (i.e. ions), electrons, and neutral species. During processing, the polymer surface is thus exposed to a highly reactive plasma, and both chemical and physical processes occur on the exposed surface areas.

It is found that repeated DBDs in air result in considerable fatigue of the effective polarization and of the piezoelectricity because of plasma-surface interactions at the internal void surfaces [38]. The fatigue is attributed to plasma-induced chain scission and oxidation of the polymer surface. Conventional DBD treatment of PP leads to the formation of polar water-soluble low-molecular-weight oxidized material (LMWOM) on the surface, containing O-C=O, C=O, and C-O groups. For cellular PP ferroelectrets, chain scission and the formation of polar LMWOM at the internal surfaces during DBDs deteriorate the chargeability of the voids, resulting in the observed polarization fatigue (Figure 12). A threshold peak-to-peak voltage V_{pp} of 3 kV for fatigue is in good agreement with the previous finding that the DBDs inside the voids are initiated when the voltage is higher than 3 kV [17]. The fatigue rate strongly depends on the amplitude and the number of driving-voltage cycles, whereas the frequency and the waveform do not have a strong influence, which indicates the influence of molecular dynamics and physico-chemical processes at the internal polymer surfaces.

7 CONCLUSION

Internally charged polymer foams and void-containing polymer systems (often called ferro- or piezoelectrets) are new members of the family of piezo-, pyro- and ferroelectric polymer electrets. They have attracted considerable attention due to their large piezoelectricity combined with high mechanical flexibility and good elastic compliance. Although these soft polymer materials are non-polar, they contain gas-filled voids that can be internally charged by means of dielectric barrier discharges (DBDs) under high electric fields. Space charge of opposite polarity is separated during DBDs and deposited at the top and bottom inner surfaces of the voids, respectively. The charged voids can be considered as man-made macroscopic dipoles, whose direction can be reversed under sufficiently high electric fields.

DBD charging of the voids is an essential process for turning polymer foams into ferroelectrets. There is a threshold voltage V_{th} for triggering the DBDs, which is found from Townsend's model of Paschen breakdown. The DBD charging is a self-extinguishing process because the electric field of the internally trapped charges partly compensates the externally applied field. Above the threshold, the effective polarization σ_{eff} increases with increasing external voltage V . If the electric field induced by the trapped charges becomes higher than the threshold value, back discharges occur when the charging voltage is sufficiently reduced or completely turned off. Consequently, a saturation of σ_{eff} is observed when the external voltage V reaches $2 V_{th}$ (twice the threshold voltage).

From the transient light emission of the DBDs in cellular PP ferroelectrets, a schematic model for the DBD charging process is developed, and the electric field during charging is estimated. The effective polarization (macroscopic dipole density) shows a hysteresis as a function of the charging voltage. The efficiency of DBD charging strongly depends on the geometry (in particular the height) of the voids, the type of gas and the gas pressure inside the voids. Furthermore, the chargeability of the voids is influenced by the plasma treatment of the inner surfaces during the DBDs. At least for cellular PP ferroelectrets, repeated DBDs in atmospheric conditions lead to considerable fatigue of the effective polarization and of the resulting piezoelectricity.

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