

Spectroscopic study of dielectric barrier discharges in cellular polypropylene ferroelectrets

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The transient light emission from the dielectric barrier discharges (DBDs) in cellular polypropylene ferroelectrets subjected to high electric poling fields was spectroscopically measured. The spectrum shows strong emission from the second positive system of molecular nitrogen, $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$, and the first negative system of N_2^+ , $N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_g^+)$, consistent with a DBD in air. When a dc voltage is applied stepwise to the ferroelectret film, light emission starts above a threshold, coinciding with the threshold voltage in obtaining piezoelectricity. From selected vibronic band strength ratios, the electric field in the discharge was determined and found to agree with Townsend breakdown. © 2007 American Institute of Physics. [DOI: 10.1063/1.2786597]

Cellular polymers (polymer foams) were produced as early as the 1960s.¹ They are now widely used in daily life for thermal insulation, shock and sound absorptions, packaging, etc.² In recent years, a number of nonpolar cellular or porous polymers were discovered to exhibit a strong electromechanical (quasipiezoelectric) response. These materials are now more and more called “ferroelectrets.”^{3,4} In order to render ferroelectrets piezoelectric, their voids must be internally charged by means of micro-plasma discharges.^{5–8} This charging process represents dielectric barrier discharges (DBDs), (also referred to as barrier discharges). In DBDs, at least one side of the discharge gap is insulated from the electrodes by a dielectric layer. DBDs are widely used for ozone generation, for surface treatment, for pollution control, for excimer lamps, and for plasma display panels, and have attracted extensive research.⁹ While the theoretical analysis of the piezoelectricity of ferroelectrets, the dependence of the piezoelectricity on the morphology, and the development of ferroelectrets based on new materials have been the subject of numerous publications in recent years, relatively little is known about the DBD process in the voids of ferroelectrets.

DBDs in ferroelectrets during charging are accompanied by light emission that can be photographed with a digital camera.^{5,6} This light emission arises from electronically excited and/or ionized gas molecules inside the voids and can be used as a diagnostic tool for characterizing the DBDs.¹⁰ In this letter, the transient light emission from the DBDs in cellular polypropylene (PP) ferroelectrets subjected to high electric fields was quantitatively and spectroscopically analyzed.

Samples were prepared from commercial cellular PP films with the trade name PQ50 (Nan Ya Plastics Corporation, Taiwan, China). They are produced by stretching filler-loaded PP under suitable conditions.¹¹ The initial thickness and density are 50 μm and 550 kg/m^3 , respectively. In order to optimize their electromechanical properties, the samples were inflated by a gas diffusion expansion in nitrogen and a subsequent heat treatment.¹² The samples were then metalized on both sides with semitransparent gold electrodes having a diameter of 16 mm and a thickness of 20 nm. The edges of the electrodes were covered with silicone rubber in

order to suppress corona discharges at the periphery of the electrodes. All experiments were performed in a light-tight chamber. Light emission was recorded by a photomultiplier (R7205-01, Hamamatsu) from one side of the sample. The photomultiplier tube (PMT) signal was captured by a digital storage oscilloscope (Agilent 54833A). The charging voltage was supplied by a high voltage amplifier (Trek, Model 610) controlled by an arbitrary waveform function generator (HP 33120A). The optical emission spectra of the light emission were recorded with a fiber-optic charge-coupled device spectrometer (Andor Technology), which consists of an optical fiber, a monochromator, and a charge-coupled device (CCD) camera (Model DU420A-OE). In order to block any light originating from a corona discharge at the electrode edge, the side of the sample facing the PMT (optical fiber) was covered by a plastic mask with a central circular hole 8.5 mm in diameter.

For ferroelectrets, it is known that the curve of the piezoelectric d_{33} coefficient versus charging voltage shows a threshold behavior.⁶ The piezoelectric activity significantly increases with the increase of charging voltage when the latter is higher than the threshold value. The same behavior was found for the light emission during charging, as shown in Fig. 1, in which a stepwise voltage waveform was applied to the sample. Light emission is observed when the charging

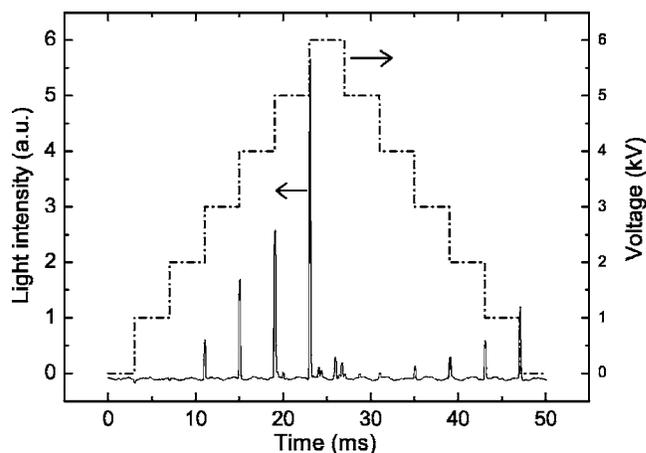


FIG. 1. PMT signal as a function of time under stepwise charging voltages. The charging voltage is increased and then decreased in steps of 1 kV.

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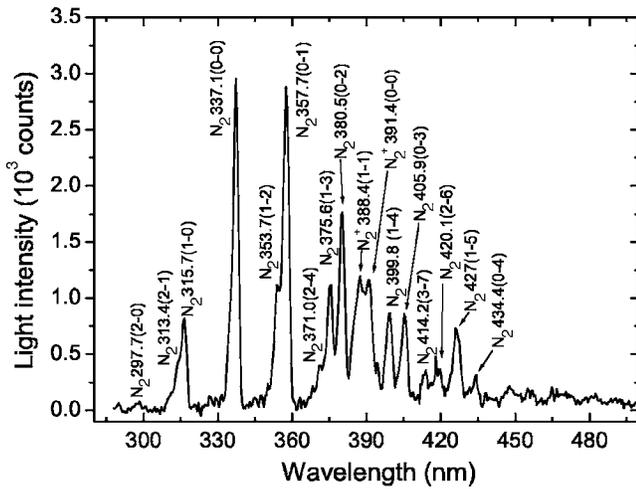
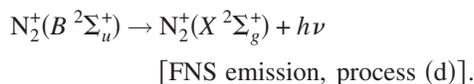
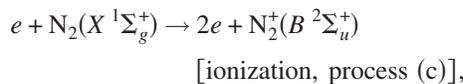
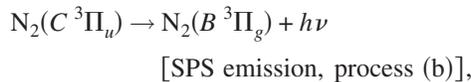
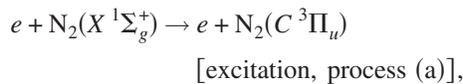


FIG. 2. Optical emission spectra of PQ50 ferroelectret under positively biased sinusoidal voltages with a frequency of 100 Hz and V_{pp} of 6 kV. The CCD camera is internally triggered with an exposure time of 4 s.

voltage reaches 3 kV, and thereafter the light intensity significantly increases with the increase of voltage. As can be seen from Fig. 1, the light emission occurs only at the beginning of each relevant voltage step and decreases very quickly back to the noise level of the PMT. This is attributed to the choking effect in DBDs.⁹ In addition, measurable light emission starts again when the voltage decreases from the maximum of 6 kV back to about 3 kV. This emission is caused by a back discharge.⁸

Analysis of the optical emission spectrum (OES) is an effective method for diagnosing DBDs. The OES of the DBDs in cellular PP ferroelectrets was recorded within the wavelength range of 250–700 nm. A part of the spectrum from samples under positively biased sinusoidal voltages $V = \frac{1}{2}V_{pp}[1 + \sin(\omega t)]$ is presented in Fig. 2. There is no detectable optical emission when V_{pp} is lower than 3 kV, which is in agreement with the PMT results. Above 3 kV, the optical emission spectra can be clearly measured. They consist of vibronic bands of the second positive system (SPS) of molecular nitrogen (N_2) and the first negative system (FNS) of N_2^+ , which is consistent with DBDs in air.¹³

The optical emission results from the following elementary processes:^{13,14}



The SPS of N_2 originates from processes (a) and (b). Obviously, it does not contribute to charge separation, since it only involves electronically excited neutral N_2 molecules, whereas the appearance of the FNS of N_2^+ [processes (c) and (d)] indicates the ionization of molecular nitrogen. Since in-

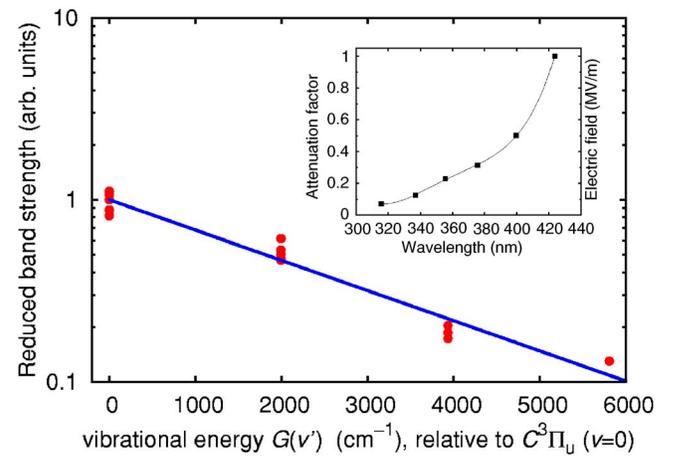


FIG. 3. (Color online) Boltzmann plot of the SPS reduced band strengths [i.e., $I/(C_{v'-v''}q_{v'v''}v^3)$, shown as solid circles] and a least squares fit (straight line) corresponding to a vibrational temperature of 3700 K. The inset shows the optical attenuation coefficient $C_{v'-v''}$ as a function of wavelength normalized to C_{-4} .

dividual rotational lines cannot be resolved by the spectrograph, the vibronic band intensity can be written as¹⁵

$$I = C(v)q_{v'v''}v^3 \exp\left(-\frac{G(v')hc}{kT_{\text{vib}}}\right), \quad (1)$$

where I is the light intensity in counts, T_{vib} is the vibrational temperature, and h , c , and k are Planck's constant, the speed of light and Boltzmann's constant, respectively. For the SPS, the Franck-Condon factors $q_{v'v''}$ (where v' and v'' are the vibrational quantum numbers of the upper and lower level, respectively), the transition frequencies ν , and the vibrational term values $G(v')$ were taken from Ref. 14. $C(v)$ is a proportionality factor which, for a calibrated spectrometer, should be independent of ν . However, a comparison of the experimental spectrum with simulations using Eq. (1) showed a significant intensity decrease toward shorter wavelengths, even though the spectral sensitivity of the apparatus was normalized by means of a calibrated tungsten lamp, and the wavelength-dependent absorption of the semitransparent gold electrodes¹⁶ was taken into account. We attribute this intensity decrease to absorption by UV-absorbing additives which are frequently found in PP, as well as light scattering in the cellular PP film. To determine the attenuation coefficient as a function of wavelength, $C(v)$ was approximated by a set of attenuation coefficients $C_{v'-v''}$. Thus, there is one coefficient for each group of bands with constant $v'-v''$ (and very similar wavelengths). These coefficients, as well as $T_{\text{vib}} \approx 3700$ K, were determined by fitting the observed band strengths to Eq. (1). The reduced band strengths [i.e., $I/(C_{v'-v''}q_{v'v''}v^3)$] are shown in Fig. 3 as a Boltzmann plot; the inset shows the attenuation coefficients (normalized to C_{-4}).

With the known attenuation coefficients (interpolated by a fourth order polynomial), absorption-corrected intensities of the N_2 SPS (0→0) and (2→5) bands (at 337.1 and 394.3 nm, respectively) and the N_2^+ FNS (0→0) band at 391.4 nm were calculated. Their ratios, subsequently denoted as $R_{391/337}$ and $R_{391/394}$, have been shown to be an indicator of the electric field in air discharges,¹⁷ as the ionization process (c) of molecular nitrogen is field dependent. Figure 4 shows the intensities of the N_2 SPS (0→0) and N_2^+ FNS (0→0)

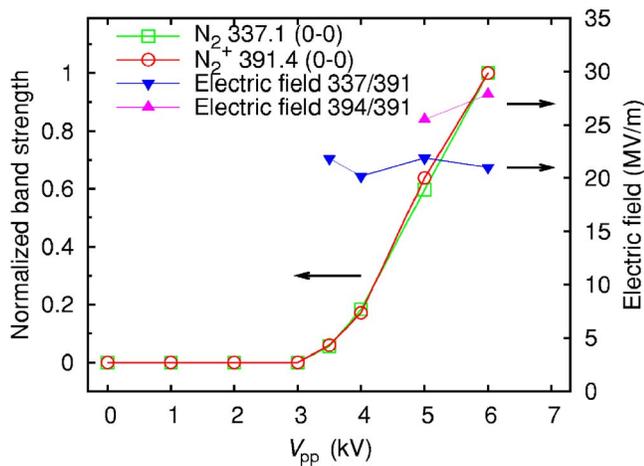


FIG. 4. (Color online) Spectral intensities of the N_2 SPS (0-0) band at 337.1 nm and the N_2^+ FNS (0-0) band at 391.4 nm as a function of V_{pp} (open squares and circles). The band strengths were normalized to their respective maximum value at $V_{pp}=6$ kV. Also shown are the electric field strengths calculated from the $R_{391/337}$ and $R_{391/394}$ intensity ratios (upward and downward triangles).

bands as a function of V_{pp} . Both bands appear in the spectrum when V_{pp} reaches 3 kV and then significantly increase with V_{pp} , exhibiting a very similar dependence on V_{pp} . This behavior is in good agreement with the dependence of the piezoelectric d_{33} coefficient on the charging voltage.⁸ Using the empirical equations of Paris *et al.*,¹⁷ the $R_{391/337}$ and $R_{391/394}$ ratios were used to determine the electric field in the voids at the moment of discharge (also shown in Fig. 4). Both ratios give an electric field between 21 and 28 MV/m without a significant dependence on V_{pp} . These values are in good agreement with the breakdown strength in air according to the Townsend breakdown model¹⁸ for air-filled voids with heights between 10 and 15 μm . Smaller voids should have a higher breakdown strength and would therefore experience breakdown at higher values V_{pp} , suggesting that the observed electric field should rise with V_{pp} . On the other hand, this dependence would be mitigated by their smaller contribution to the overall light emission (due to their smaller size), and the fact that the larger voids may experience a secondary breakdown at higher applied voltages,⁸ which would happen at the same, lower value of the external voltage as the first breakdown. Thus, the spectroscopic measurements of the breakdown field strengths are biased toward larger voids.

In conclusion, the optical emission spectrum of the DBDs in ferroelectrets shows strong UV/visible emission resulting from the second positive system (SPS) of molecular nitrogen $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ and the first negative system (FNS) of $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$, consistent with DBDs in air.

The transient light emission from the DBDs in cellular polypropylene ferroelectrets subjected to high electric fields shows the same trend as the piezoelectricity and is therefore strongly correlated with it. From a spectroscopic analysis of the band strength ratios, the electric field during the discharge process could be determined to be in the range between 21 and 28 MV/m, in good agreement with the Townsend breakdown model. Further studies with an improved spectroscopic setup are expected to yield a better signal-to-noise ratio. These measurements will thus become an important step toward developing a model of the charging process. This in turn will lead to further optimizations of the underlying DBD process and thus also of the poling of cellular ferroelectrets.

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- ¹L. J. Gibson and M. F. Ashby, *Cellular Solids: Structure and Properties*, 2nd ed. (Cambridge University Press, Cambridge, 1997), Chap. 1.
- ²*Handbook of Polymeric Foams and Foam Technology*, edited by D. Klempner and K. C. Frisch (Hanser, Munich, 1991).
- ³S. Bauer, R. Gerhard-Mulhaupt, and G. M. Sessler, *Phys. Today* **57**(2), 37 (2004).
- ⁴M. Wegener and S. Bauer, *ChemPhysChem* **6**, 1014 (2005).
- ⁵M. Lindner, S. Bauer-Gogonea, S. Bauer, M. Paajanen, and J. Raukola, *J. Appl. Phys.* **91**, 5283 (2002).
- ⁶M. Wegener, M. Paajanen, W. Wirges, and R. Gerhard-Mulhaupt, *Proceedings of the 11th International Symposium on Electrets, Melbourne, Australia, 1-3 October 2002* (IEEE Service Center, Piscataway, NJ, 2002) pp. 54-57.
- ⁷S. Zhukov and H. von Seggern, *J. Appl. Phys.* **101**, 084106 (2007).
- ⁸X. Qiu, A. Mellinger, M. Wegener, W. Wirges, and R. Gerhard, *J. Appl. Phys.* **101**, 104112 (2007).
- ⁹U. Kogelschatz, *Plasma Chem. Plasma Process.* **23**, 1 (2003).
- ¹⁰I. Graz (private communication).
- ¹¹A. Savolainen and K. Kirjavainen, *J. Macromol. Sci., Chem.* **A26**, 583 (1989).
- ¹²M. Paajanen, H. Minkinen, and J. Raukola, *Proceedings of the 11th International Symposium on Electrets, Melbourne, Australia, 1-3 October 2002* (IEEE Service Center, Piscataway, NJ, 2002), pp. 191-194.
- ¹³K. V. Kozlov, H. E. Wagner, R. Brandenburg, and P. Michel, *J. Phys. D* **34**, 3164 (2001).
- ¹⁴A. Lofthus and P. H. Krupenie, *J. Phys. Chem. Ref. Data* **6**, 113 (1977).
- ¹⁵G. Herzberg, *Molecular Spectra and Molecular Structure. I: Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), Chap. IV.
- ¹⁶*CRC Handbook of Chemistry and Physics*, edited by David R. Lide and H. P. R. Frederikse, 75th ed. (CRC Press, Boca Raton, 1995), Chap. 12, p. 121.
- ¹⁷P. Paris, M. Aints, F. Valk, T. Plank, A. Haljaste, K. V. Kozlov, and H. E. Wagner, *J. Phys. D* **38**, 3894 (2005).
- ¹⁸John M. Meek and John D. Craggs, *Electrical Breakdown of Gases* (Oxford University Press, London, 1953), Chap. I.