PACS 77.84.-s, 73.61.Ph, 77.55.Kt

Fedosov SN, Sergeeva AE

Odessa National University of Technology, vul. Kanatna 112, Odessa, 65039, Ukraine,
e-mail <snfedosov@ukr.net>

USING THE PYROELECTRIC RESPONSE TO STUDY THE POLARIZED STATE IN A TYPICAL FERROELECTRIC POLYMERS

This article examines the correlation between the pyroelectric response in typical films of ferroelectric polymers and the value of the residual ferroelectric polarization. The pyroelectric response was obtained by the thermal pulse method proposed by Collins. The magnitude of the residual polarization was measured depending on the magnitude of the applied electric field during primary electrification (poling) and during its switching. It is shown that the used method has the high sensitivity. It was found that the magnitude of the pyroelectric response depends significantly on the polarized state, which is determined by the values of the electric field during electrification and polarization switching and on the duration of exposure to this field. The identity of the graphs of the dependence of the residual polarization on the field and time and the corresponding graphs of the magnitude of the pyroelectric response led to the final conclusion about the proportionality of the magnitude of the response to the residual polarization. Thus, it is concluded that the pyroelectric response method can be used to estimate the magnitude of polarization in ferroelectric polymers.

Introduction

Ferroelectric polymers, in particular polyvinylidene fluoride (PVDF) and its copolymers with tetrafluoroethylene P(VDF-TFE) and trifluoroethylene P(VDF-TrFE), have been considered for a number of years as an alternative material for replacing ceramic ferroelectrics in production of various types of sensors and electromechanical converters [1].

The most important parameter of such materials is the magnitude and stability of the residual ferroelectric polarization *P*. Such polarization is created in original materials, usually thin films, by electrifying (poling) them in a strong DC electric field, which is carried out either by the sandwich method (a polymer film is located between two metal electrodes [2]), or under the action of corona discharge [3].

Performance characteristics of the finite elements, such as the piezoelectric and pyroelectric coefficients, depend on the magnitude of the residual polarization.

At the same time, it is known that the magnitude of the residual polarization in ferroelectric polymers depends on the value of the applied electric field during poling, as well as on the duration of poling, and on temperature [4].

It is also known that a part of the formed residual polarization can be switched back, if the conditions for neutralizing the depolarizing field, which inevitably arises during electrification, are not provided [5].

Given the above, it is clear how important to know the magnitude of the polarization. Unfortunately, the known methods for determining the value of the residual polarization are rather complicated and cumbersome. The most commonly used method is to construct a hysteresis curve in the coordinates of the dependence of polarization on the changing electric field [6]. The Sawyer-Tower method [7] often used in the study of ceramic ferroelectrics for obtaining dielectric hysteresis loops at frequency of 1 kHz is not suitable for ferroelectric polymers because of the long relaxation time in such polymers [8]. To obtain the correct polarization values, measurements must be carried out at infra-low frequencies during long time.

The purpose of this article is to prove that the dependences of the polarization value on the field strength and the poling time in ferroelectric polymers correlate with similar dependences of the pyroresponse obtained by the heat pulse method.

The carried out experimental studies confirm this position, which allows us to recommend the pyroresponse method for the rapid

determination of the value of ferroelectric polarization in ferroelectric polymers.

Pyroelectricity in ferroelectric polymers

Pyroelectric effect in PVDF films was discovered more than 40 years ago. However, despite the large number of works, the nature of pyroelectricity in PVDF still remains unclear. A series of papers were devoted to the pyroelectric properties of the ferroelectric polymers, the results of which are summarized in reviews [10-13] that describe the main proposed models of pyroelectricity in PVDF. It is stipulated in all models that electrostriction, fluctuation of dipoles and change in the dimensions contribute to the pyroelectricity.

Under the pyroelectric effect, one means the range of phenomena associated with reversible changes in the electric displacement D vector (induction) when the temperature changes. Since induction depends on the internal polarization P, then for the case of a flat short-circuited sample with homogeneous polarization P we obtain

$$p_o = \frac{\partial D}{\partial T} = \frac{\partial P}{\partial T} = \frac{\partial \sigma}{\partial T} = \frac{\partial (q/S)}{\partial T}, \qquad (1)$$

where p_o is the pyroelectric coefficient, q and σ are magnitude and density of the bound surface charge; S is the surface area.

In the experimental conditions, the current $I(T) = \frac{\mathrm{dq}}{\mathrm{dt}}$ is measured occurring when the temperature change (dT/dt), and the pyrocoefficient p is considered to have the following value

$$p = \frac{1}{S}\frac{\mathrm{dq}}{\mathrm{dT}} = \frac{1}{S}\frac{I(T)}{\mathrm{dT}/\mathrm{dt}}. \qquad (2)$$

Investigating the pyroelectric effect in PVDF, Lines and Glass [8] came to the conclusion that this is a real pyroelectricity, but not a depolarization effect observed in many polar electrets, because the crystalline phase of PVDF completely corresponds to the definition of a ferroelectric, as a pyroelectric with reversible spontaneous polarization under application of the electric field.

Fedosov and von Seggern [4,14,15] proved that compensating charges localized on the surface of crystallites are very important in two-component ferroelectric polymers of the PVDF type for obtaining high and stable polarization. It is generally accepted that the pyrocoefficient in PVDF is directly proportional to the value of the residual polarization.

Material and methods

We studied thin films of ferroelectric polymers, such as PVDF and its copolymer with tetrafluoroethylene P(VDF-TFE). Samples of PVDF and P(VDF-TFE) films having thickness of 20-30 μm were obtained from the experimental batches of "Plastpolymer", St. Petersburg, produced by the method of extrusion, followed by uniaxial orientation (stretching) in the ratio 1:4 at the temperature of 100 °C followed by annealing at 120 °C for 1 hour. The degree of crystallinity of PVDF and P(VDF-TFE) films according to the manufacturer was (47 ± 3) %. The crystallites sizes according to the results of X-ray analysis have the following values: L_α = 96±6 Å, L_β = 70±8 Å. The percentage of tetrafluorethylene in P(VDF-TFE) was 5-10%.

Biaxually oriented PVDF films of the Kureha Co. had a thickness of 12.5 μm. In order to determine the relation between non-polar α-phase and ferroelectric β-phase, transmission and reflection spectra of all types of films in the range of 400-650 cm^{-1} were studied using the IR spectrometer FT-IR Perkin-Elmer 1750 with Fourier transform. Judging by the magnitude of 535 and 510 cm^{-1} peaks, it was found that the ratio 43:57 was between α and β in PVDF (Plastpolymer) films, 30:70 in Kureha Co. films, and 5: 95 in P(VDF-TFE) films.

The pyroelectric effect is usually investigated in quasi-static or dynamic mode. In the first case, the pyroelectric current is measured during the slow heating of the short-circuited sample, while in the second case, the variable component of the current is studied during a rapid change of temperature. The main difficulties of the quasi-static method are the separation of the pyroelectric (reversible) component of the thermal shock from the relaxation (irreversible) component in the Thermally Stimulated Depolarization (TSD) current.

We measured the pyroelectric dynamic coefficient by the thermal pulse method developed by Collins [16] and used in a number of other studies.

The light pulse of 50 μs duration was gener-

ated using the Metz 45 CT-3 flashlight and was used as a reproduced heat source that penetrates the surface of the poled films. The pyroelectric signal was recorded using a broadband Tektronix TDS 510A. oscilloscope. This method is the dynamic one.

With the help of a highly sensitive pyroelectric sensor it was established that light pulses are characterized by a rather high reproducibility. The average energy scatter in measuring of 200 consecutive pulses was 2.4%. The magnitude of the pyroelectric coefficient was judged by the maximum value of the electric signal. Thus the results were obtained in relative units.

Dependence of the residual spontaneous polarization on electric field and poling time was studied on samples of PVDF by the method of poling and switching of polarization described in details in works of Fedosov and von Seggern [4,14,15]

Results and discussion

Pyroelectric studies of PVDF films have an independent value, since PVDF is widely used in pyroelectric sensors. However, it is interesting to study pyroactivity in conjunction with the residual ferroelectric polarization, because it will allow on one side to clarify the nature of the pyroelectricity in PVDF, and on the other to ensure its stability.

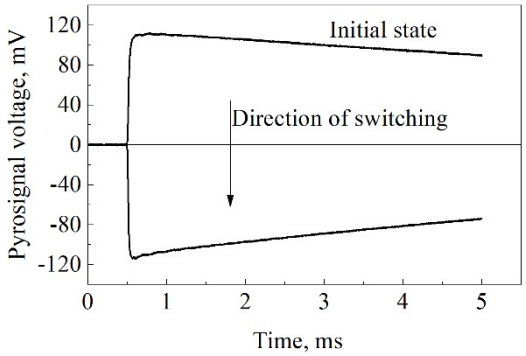

Fig. 1. The pyroelectric signal after the polarization switching of PVDF film by applying 2 kV voltage for 50 seconds. Pyroelectricity was measured after 1.5 min after the voltage switching off.

Measurement of the pyroactivity by the Collins method was carried out immediately after poling or polarization switching. Fig. 1 shows how the pyroelectric signal changes when the polarization is fully switched from a fully polarized state. Although the value of the pyrocoefficient can only be judged in relative units, it is evident that the sensitivity of the method is rather high and the signal is completely symmetric after the full switching. In Fig. 2 it is shown that full switching occurs only if the voltage pulse duration exceeds 100 s. At a shorter duration of the voltage pulse, there is only a partial switching of polarization judging from the data of Fig. 2.

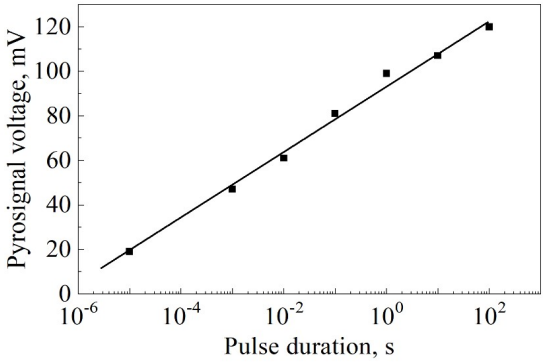

Fig. 2. Dependence of the pyroelectric signal on the duration of the polarizing pulse in the range from 10 μs to 100 s during initial poling of the PVDF film by 2.5 kV voltage.

Fig. 3 shows the results of four series of experiments, in which the polarization switching was performed at different durations of the voltage pulse, but with the same magnitude in each series. At a voltage of 0.5 kV (Fig. 3) that provides a field strength of about 40 MV/m, being in the same order as the coercive field, even with a pulse duration of 50 s, only 6.4% of the polarization is switched, which in principle can be switched, and if the pulse duration is shorter than 50 ms, no switching is practically happening.

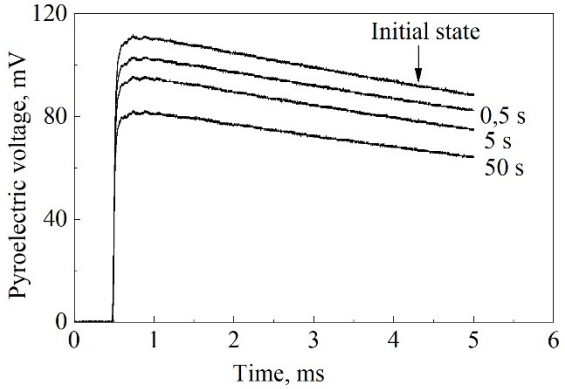

Fig. 3. Pyrosignal at sequential polarization switching in PVDF films by pulses of 0.5 kV voltage with duration from 5 ms to 50 s. The duration of the voltage pulse is indicated near the curves.

At the voltage of 1 kV applied for 50 s, 44.4% of the residual polarization is switched, that is, the sample is almost converted to the state with zero mean polarization. At this voltage, the 2.2% polarization is switched even within 50 μs of the switching voltage application. Increasing the voltage to 1.5 kV leads to the switching of 79.4% of the residual polarization by 50 s application of voltage.

At a voltage of 2 kV for 50 s, the polarization is completely switched. It is interesting to note that the specific shape of the pyroelectric signal when switched polarization is more than 50%, that is, when the direction of the average predominant orientation of the dipoles changes to the opposite direction.

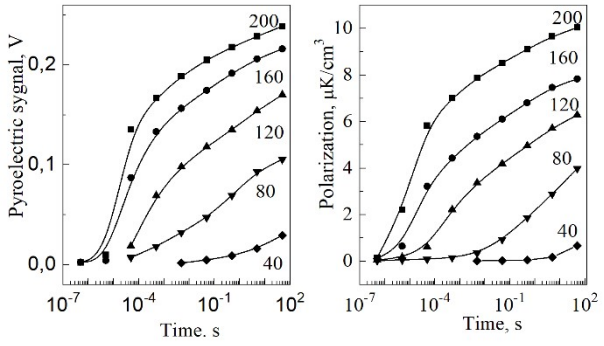

Fig. 4. Evolution of pyroelectric activity and stable ferroelectric part of polarization obtained by sequential application of switching voltage pulses with increasing duration from 0.5 μs to 50 s and at different field strength.

In the electrode zone, which the thermal pulse passes during t_o = 0.2 ms, when the polarity direction changes to the opposite, a nonsymmetric in shape pyroelectric signal is formed in relation to the initial one. In the vicinity of the electrode, the direction of the pyroelectric signal change is maintained during the switching of polarization indicating the existence of a near-to-electrode layer of thickness about $x=\sqrt{\lambda t_o}$ where λ is the thermal conductivity of PVDF. According to the literature data, the coefficient of thermal conductivity of PVDF is $\lambda = 6\cdot10^{-8}$ m^2/s, thus the thickness of the electrode layer is of the order of 3 μm. We believe that the feature revealed by us is due to the fact that the originally formed polarization in this layer does not switch even in high fields [17].

It is natural to assume that polarization near the electrode does not increase sharply, but there is some transition layer in which the polarization grows from zero at the electrode to a maximum uniform value in the volume of the film.

According to the Poisson equation, inhomogeneous polarization in any layer can be stable only with the presence of a compensating charge in this layer [15]. Apparently, this charge was trapped by deep traps and not released during the polarization switching. The revealed phenomenon is similar to the established by us feature about impossibility of improving the polarization uniformity if its initial formation took place in weak or medium fields [17].

It was found that polarization switched under the action of several successive short voltage pulses is much smaller than the polarization switched by one pulse of the duration equal to the total time of several short pulses. This indicates that there is some distribution of switching times, i.e. some dipoles are easily switched, while others require more time to be switched. Under the influence of short voltage pulses, only "fast" dipoles are switched, while during the continuous voltage application both "fast" and "slow" dipoles are switched, so the total switched polarization significantly increases.

All described experiments were carries out on PVDF and P(VDF-TFE). It was found that obtained results were identical for both kinds of samples.

Conclusion

In this paper, polarization switching at different times and field strength is compared with the values of the pyroelectric signal under the same poling and switching conditions. The absolute similarity of the above experimental graphs indicates that there is a direct proportional relationship between the residual ferroelectric polarization and the value of the pyroelectric coefficient in the studied ferroelectric polymer. This provision makes it possible to use the technically simple pyrocoefficient measurement to evaluate the polarized state of poled ferroelectric polymer films, that is, to estimate the magnitude and the direction of the residual polarization.

References

1. Sessler G. M. Electrets: Recent Developments // J. Electrostatics – 2001, - v.51, No. 2 – p. 137-145.
2. von Seggern H, Fedosov S. N. Conductivity induced polarization in a semicrystalline ferroelectric polymer // IEEE Trans. Diel. Elect. Insul. – 2004. – v. 11, No. 2. – p. 232– 241.
3. Fedosov S. N., Sergeeva A. E. Corona poling of ferroelectric and nonlinear optical polymers // Moldavian Journal of the Physical Sciences, 2002, No.2, p.28-31.
4. Fedosov S. N., von Seggern H. Pyroelectricity in polyvinylidene fluoride: influence of polarization and charge // J. Appl. Phys. – 2008. – v. 103, No.1. – p. 014105–014109.
5. Fedosov S. N., von Seggern H., Back-switching of ferroelectric polarization in two-component systems // J. Appl. Phys. – 2004. – v. 96, No. 4. – p. 2173–2180.
6. Furukawa T., Nakajima T., Yoshiyuki T., Factors Governing Ferroelectric Switching Characteristics of Thin VDF/TrFE Copolymer Films // IEEE Transactions on Dielectrics and Electrical Insulation – 2006, v. 13, No. 5 - p.1120-1131.
7. Stewart M., Cain M. G., Weaver P. Electrical Measurement of Ferroelectric Propertie // in Characterisation of Ferroelectric Bulk Materials and Thin Films (ed. Cain M. G.), Springer, 2014, 280 p.
8. Lines M. E. and Glass A. M., Principles and Applications of Ferroelectrics and Related Materials (Oxford University Press, Oxford, Science - 2001), 680 p.
9. Mort J. Polymers, Electronic Properties // in Encyclopedia of Physical Science and Technology (Third Edition), 2003.
10. Stewart M., Cain M. G., Weaver P. Electrical Measurement of Ferroelectric Propertie // in Characterisation of Ferroelectric Bulk Materials and Thin Films (ed. Cain M. G.), Springer, 2014, 280 p.
11. Fukada E. History and Recent Progress in Pyroelectric Polymer // IEEE Trans. Ultrason. Ferroelectrics and Freq. Control. – 2000. – v.47, No. 6. –p.1277–1290.
12. Bauer S., Bauer-Gogonea S., Lindner M., Schrattbauer K. Piezo-, Pyro- and Ferroelectric Polymers. In: Galassi C. (eds) Advances in Science, Technology and Applications. NATO Science Series, Springer, Dordrecht, 2000, vol 76.
13. Lang S. B., Muensit S. Review of some lesser-known applications of piezoelectric and pyroelectric polymers // Appl. Phys. 2006, - v. A 85, p. 125–134.
14. von Seggern H., Fedosov S. N. Conductivity-induced polarization buildup in PVDF // Appl. Phys. Lett. 2002, v. 81, No. 15. – p. 2830–2832.
15. von Seggern H., Fedosov S. N. Importance of screening charge dynamics on polarization switching in polyvinylidene fluoride // Appl. Phys. Lett. – 2007. – v. 91, No. 6. – p. 62914–62918.
16. Raju G. G. The Thermal Pulse Method of Collins // in Dielectrics in Electric Fields, CRC Press, 2003, p. 520-525
17. Fedosov S. N., Sergeeva A. E. Distribution of the Ferroelectric Polarization in PVDF During Initial Poling and Polarization Reversal // J. Nano- Electron. Phys. – 2019, v. 11, No 1, 01012 (7pp).

PACS 77.84.-s, 73.61.Ph, 77.55.Kt

Fedosov S. N., Sergeeva A. E.

USING THE PYROELECTRIC RESPONSE TO STUDY THE POLARIZED STATE IN A TYPICAL FERROELECTRIC POLYMERS

Summary

In the presented paper, the correlation between the pyroelectric response in typical films of ferroelectric polymers PVDF and P(VDF-TFE) and the value of the residual ferroelectric polarization was investigated. The pyroelectric response was measured by the thermal pulse

Collins method. Dependence of the residual polarization on the value of the applied electric field during primary electrification (poling) and during its switching was also measured. It has been found that the used methods have high sensitivity and reproducibility. It was shown that the magnitude of the pyroelectric response depended significantly on the polarized state, which was determined by the values of the electric field during electrification and polarization switching and on the duration of exposure to this field. The identity and absolute similarity of the residual polarization dependence graphs on the field and time and corresponding graphs of the pyroelectric response magnitude led to the conclusion that the magnitude of the pyroelectric was proportional to the residual polarization. Thus, the pyroelectric response method can be used to estimate the value of the residual polarization in ferroelectric polymers.
Key words: ferroelectric polymers, pyroelectricity, residual polarization

PACS 77.84.-s, 73.61.Ph, 77.55.Kt

Федосов С.Н., Сергєєва О.Є.

ВИКОРИСТАННЯ ПІРОЕЛЕКТРИЧНОГО ВІДГУКУ ДЛЯ ДОСЛІДЖЕННЯ ПОЛЯРИЗОВАННОГО СТАНУ У ТИПОВИХ СЕГНЕТОЕЛЕКТРИЧНИХ ПОЛІМЕРАХ

Резюме

У представленій роботі досліджено кореляцію між піроелектричним відгуком у типових плівках сегнетоелектричних полімерів ПВДФ та П(ВДФ-ТФЕ) та величиною залишкової поляризації. Піроелектричну реакцію вимірювали методом Коллінза теплового імпульсу. Виміряно також залежність залишкової поляризації від величини електричного поля під час первинної електризації та під час її перемикання. Встановлено, що використані методи мають високу чутливість. Показано, що величина піроелектричного відгуку залежить від поляризованого стану, який визначався величинами електричного поля при електризації та перемиканні поляризації та від тривалості впливу поля. Тотожність та абсолютна подібність графіків залежності залишкової поляризації від поля та часу та відповідних графіків величини піроелектричної реакції дозволили зробити висновок, що величина піроелектричного відгуку була пропорційна залишковій поляризації. Таким чином, метод піроелектричного відгуку може бути використаний для оцінки величини залишкової поляризації в сегнетоелектричних полімерах.

Ключові слова: сегнетоелектричні полімери, піроелектрика, залишкова поляризація

PACS 77.84.-s, 73.61.Ph, 77.55.Kt

Федосов С.Н., Сергеева А.Е.

ИСПОЛЬЗОВАНИЕ ПИРОЭЛЕКТРИЧЕСКОГО ОТКЛИКА ДЛЯ ИССЛЕДОВАНИЯ ПОЛЯРИЗИРОВАННОГО СОСТОЯНИЯ В ТИПИЧНЫХ СЕГНЕТОЭЛЕКТРИЧЕСКИХ ПОЛИМЕРАХ

Резюме

В представленной работе исследована корреляция между пироэлектрическим откликом в типичных пленках сегнетоэлектрических полимеров ПВДФ и П(ВДФ-ТФЭ) и величиной остаточной сегнетоэлектрической поляризации. Пироэлектрическую реакцию измеряли методом теплового импульса, предложенного Коллинзом. Измерена также зависимость

остаточной поляризации от величины приложенного электрического поля при первичной электризации и при ее переключении. Установлено, что использованные методы обладают высокой чувствительностью и воспроизводимостью. Показано, что величина пироэлектрического отклика существенно зависит от поляризованного состояния, определяемого значениями электрического поля при электризации и переключении поляризации и продолжительности воздействия этого поля. Тождество и абсолютное сходство графиков зависимости остаточной поляризации от поля и времени и соответствующих графиков величины пироэлектрической реакции позволили заключить, что величина пироэлектрического отклика была пропорциональна остаточной поляризации. Таким образом, метод пироэлектрического отклика может быть использован для оценки величины остаточной поляризации в сегнетоэлектрических полимерах.

Ключевые слова: сегнетополимеры, пироэлектричество, остаточная поляризация

This article has been received in October 22, 2021.