

# МАТЕРІАЛИ ДЛЯ СЕНСОРІВ

## SENSOR MATERIALS

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### INTERRELATION BETWEEN PYROELECTRIC PROPERTIES AND RESIDUAL POLARIZATION IN POLYVINYLIDENE FLUORIDE INTENDED FOR MAKING PYROELECTRIC SENSORS

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**Abstract.** Pyroelectricity and fractional thermally stimulated depolarization currents (TSDC) were experimentally studied in polyvinylidene fluoride (PVDF) films poled by application of high DC field at room temperature. The obtained polarization is found to be less thermally stable than the correlated compensating charge. It is demonstrated by investigation of the charge balance and the pyroelectric coefficient measured during cooling in a fractional experiment, that trapped polarization-compensating charge is responsible for a partial realignment of polarization during cooling.

The polarization and the volume charges in PVDF samples poled by application of a high field at room temperature are not thermally frozen. All processes of their buildup and relaxation are interrelated. If there is any polarization, it is necessarily compensated by trapped charges.

The intention of the paper is to investigate in more depth the nature of the residual polarization in PVDF by comparing TSDC during successive heating of the poled samples to higher and higher temperatures (fractional TSDC) with pyroelectric currents obtained during the subsequent cooling the sample in each thermal cycle.

It has been found that the poled PVDF samples should be conditioned by heating to 80 °C and cooling down for obtaining the stable pyrocoefficient.

**Keywords:** pyroelectric sensors, PVDF, thermally stimulated depolarization current, ferroelectricity, polarization

#### Introduction

Solid-state sensors and detectors are widely used in measurement technology to convert non-electric physical quantities into electrical ones. One of the important areas of solid-state electronics is the development of sensors based on ferroelectric polymer films, the increased interest

in which is due to the possibility of their wide application as active elements of piezoelectric and pyroelectric sensors. The most known and promising ferroelectric polymer is polyvinylidene fluoride (PVDF) [1].

PVDF is a semicrystalline material in which ferroelectric crystallites are combined with an

amorphous phase occupying about 50% of the volume. When the melt is cooled, the molecular chains fold, forming plate-like crystals (lamellae), in which sections of macromolecular chains are arranged in a zigzag pattern [2]. The crystallites are brick-like blocks located parallel to the direction of mechanical drawing [2] having a length of 5.9–7.6 nm, a height of 2.5 nm, and a thickness of 3.7 nm. They are separated by gaps (0.4–0.7 nm) of the amorphous phase consisting of 1–3 polymer chains [3].

The polymer chain of PVDF consists of  $-\text{CH}_2-\text{CF}_2-$  units, which have a dipole moment of  $\mu=7 \cdot 10^{-30} \text{ C} \cdot \text{m}$  (2.1 D), due to the spatially symmetric arrangement of H and F atoms [2]. Polymorphism is characteristic of PVDF. In the crystallites of the  $\alpha$ -phase formed during the crystallization of PVDF from the melt [4], the chains are arranged antiparallel, and the total dipole moment per unit volume is zero, i.e. the  $\alpha$ -phase is non-polar.

When PVDF is orientationally drawn by 3–4 times [1], the  $\alpha$ -phase is partially transformed into the polar  $\beta$ -phase, which has spontaneous polarization ( $P_o=130 \mu\text{C}/\text{m}^2$ ), the direction of

which can be changed under the action of an electric field. The ratio between the  $\alpha$ - and  $\beta$ -phases depends on mechanical drawing and heat treatment [5], as well as on the electric field strength [1].

## EXPERIMENTAL DETAILS

We studied biaxially oriented ferroelectric polymer PVDF thin films from the Kureha Co. having thickness of 12.5  $\mu\text{m}$ . The degree of crystallinity according to the manufacturer was  $(47 \pm 3)\%$ . The crystallites sizes according to the results of X-ray analysis have the following values:  $L_\alpha = 96 \pm 6 \text{ \AA}$ ,  $L_\beta = 70 \pm 8 \text{ \AA}$ .

Transmission and reflection spectra of the films in the range of 400–650  $\text{cm}^{-1}$  were studied using the FT-IR Perkin-Elmer 1750 spectrometer with Fourier transform in order to determine the relation between non-polar  $\alpha$ -phase and ferroelectric  $\beta$ -phase. Judging by the magnitude of 535  $\text{cm}^{-1}$  and 510  $\text{cm}^{-1}$  peaks, it was found that the ratio 30:70 was between  $\alpha$  and  $\beta$  in Kureha Co. films and remained unchanged after poling.

The diagram of the experimental setup used in this study is shown in Fig. 1 and is described elsewhere [6].

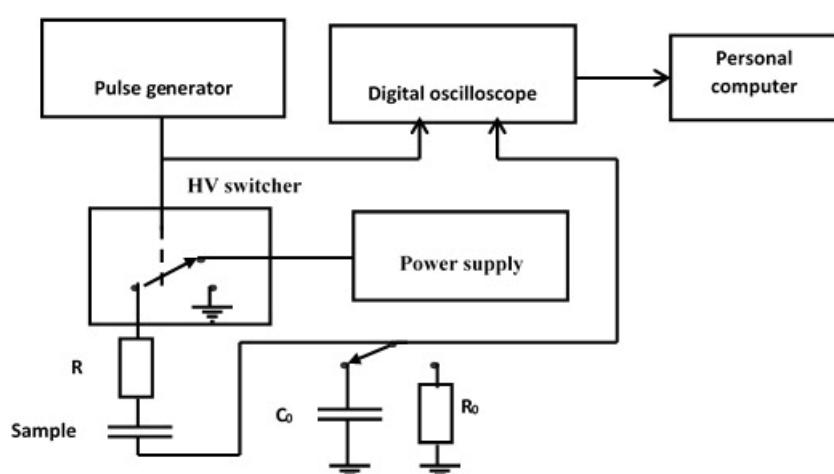


Fig. 1 Experimental setup.

Gold electrodes of  $0.2 \text{ cm}^2$  were deposited by cathode sputtering on both sides of the sample. Poling was performed at  $U_o=2 \text{ kV}$  ( $E=160 \text{ MV/m}$ ) during  $\tau=20 \text{ s}$ . The residual ferroelectric polarization  $P_r=6.1 \pm 0.2 \mu\text{C}/\text{cm}^2$  after poling was measured by processing displacement currents. Then the sample was short-circuited and

stored in the short-circuited condition for 8 h. The isothermal depolarization current was measured at  $20^\circ\text{C}$ .

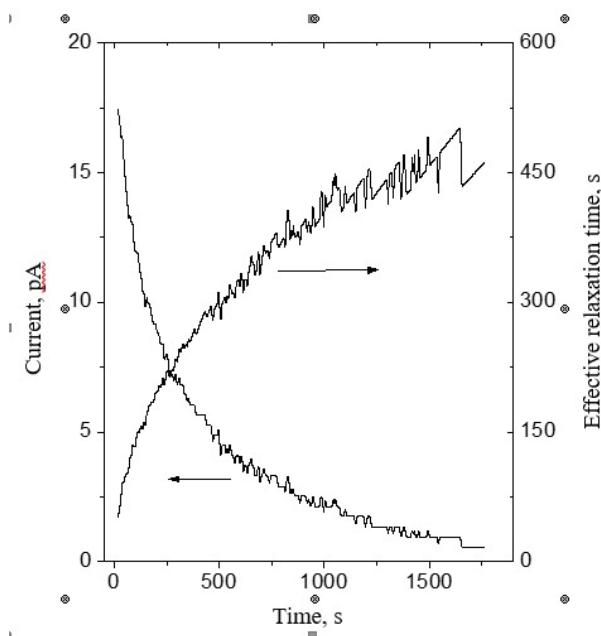
Fractional TSDC consisted in 4 sections. The samples were heated from  $20^\circ\text{C}$  with the heating rate  $\beta_h=4 \text{ K/min}$  to the maximal temperature of the section  $t_1=60^\circ\text{C}$ ,  $t_2=105^\circ\text{C}$ ,

$t_3=140$  °C and  $t_4=185$  °C. Then the samples were linearly cooled with cooling rate  $\beta_c=20$  K/min to the initial temperature of 20 °C. Pyroelectricity was measured during cooling segments of the fractions.

**ISOTHERMAL RELAXATION AFTER POLING.** If the relaxation is due to intrinsic conductivity  $g$ , the current decreases exponentially with the characteristic Maxwell relaxation time  $\tau=\varepsilon_0\varepsilon/g$ . The observed in Fig. 2 decay is not exponential, as if  $\tau$  increases with storing time.

The process can be formally characterized by the exponential decay with a time dependent relaxation time  $\tau(t)$

$$I = I_0 \exp\left(-\frac{t}{\tau(t)}\right). \quad (1)$$



**Fig. 2. Isothermal relaxation current and time dependence of the characteristic relaxation constant.**

It is seen that  $\tau$  increases from 50 to 450 s during 2000 s of storing indicating that the relaxation is caused not by the intrinsic conductivity, which would result in a constant  $\tau$ , but rather by the charge carriers injected from electrodes during poling.

After storing for a long time, the isothermal current finally decays to zero indicating that not only the average field, but also local fields become

zero everywhere in the sample. This condition has to be fulfilled before starting the TSDC experiments.

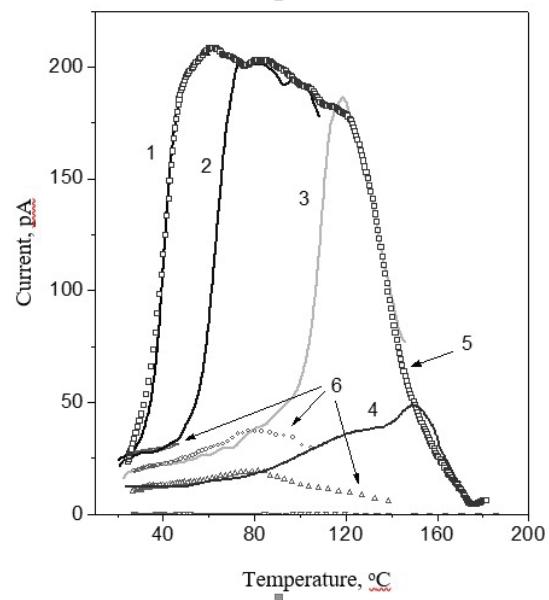
**TSD CURRENTS.** The TSD current is caused by relaxation of the residual polarization  $P$  and the compensating space charge  $\sigma$

$$I(t) = A\beta_h \left( \frac{d\sigma}{dT} - \frac{dP}{dT} \right). \quad (2)$$

Assuming that the relaxations of  $\sigma$  and  $P$  are first order processes with characteristic time constants  $\tau_\sigma$  and  $\tau_p$  and related activation energies  $E_\sigma$  and  $E_p$ , one obtains

$$I(T) = A\beta_h \left( \frac{\sigma}{\tau_\sigma \exp(-E_\sigma/kT)} - \frac{P}{\tau_p \exp(-E_p/kT)} \right). \quad (3)$$

By analyzing the expressions (1–3) and TSD currents shown in Fig. 3 we made the following conclusions:



**Fig. 3. Fractional TSD currents (1–4) measured during the heating fractions. Also shown are (5) overall TSD and (6) the pyroelectric currents.**

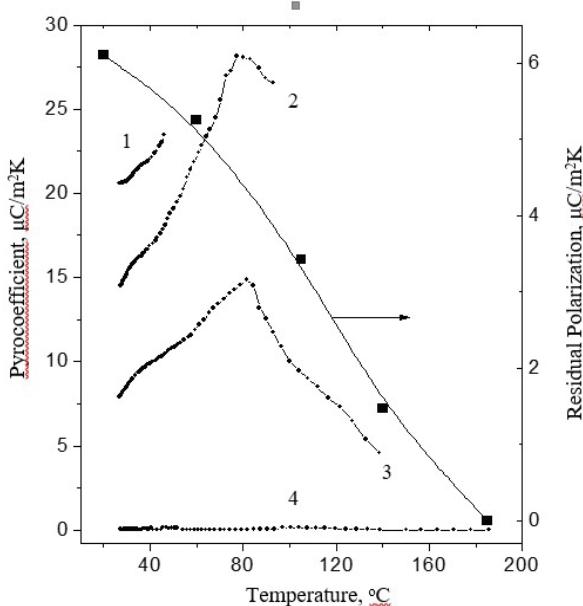
– The TSD current at any moment reflects the interrelation between  $\sigma(T)$  and  $P(T)$ .

– The direction of the TSDC is opposite to the poling current, so dipoles are less stable than the trapped charges. The relaxation process is controlled by the stability of the polarization.

– If  $\sigma$  could immediately follow the decay of  $P$ , there would be not any TSD current.

– It is not appropriate to derive the value of  $P_r$  from the integral of the TSD current. Indeed,  $P_r=6.1 \mu\text{C}/\text{cm}^2$ , while the integral of the complete TSD current is only ( $1.24 \mu\text{C}/\text{cm}^2$ ).

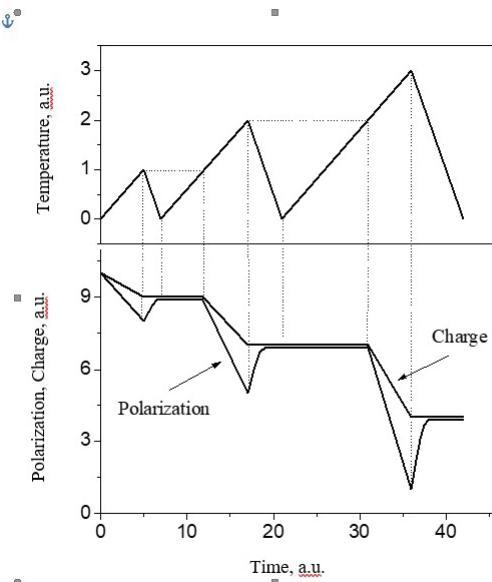
**RESIDUAL POLARIZATION AND PYROELECTRICITY.** The pyroelectric coefficient  $p$  obtained from the subsequent cycle and shown in Fig. 4 becomes lower when the poled sample is heated and cooled back down. Since  $p$  is proportional to  $P_r$ , it means that  $P_r$  irreversibly decreases with heating. The initial value of the polarization  $P_r=6.1 \mu\text{C}/\text{cm}^2$  corresponds to the pyrocoefficient  $p=25 \mu\text{C}/\text{m}^2\text{K}$ . After heating to  $60^\circ\text{C}$   $p$  decreases to  $21.5 \mu\text{C}/\text{m}^2\text{K}$  (at  $20^\circ\text{C}$ ), after the 2<sup>nd</sup> cycle  $p=14 \mu\text{C}/\text{m}^2\text{K}$ , after the 3<sup>rd</sup> one  $p=6 \mu\text{C}/\text{m}^2\text{K}$ . The data are sufficient to derive the temperature dependence of  $P_r$  shown in Fig. 4.



**Fig. 4. Pyroelectric coefficients measured during cooling fractions of the TSDC experiments compared to the temperature dependence of the residual polarization.**

It is interesting to disclose the behavior of the polarization during the fractional TSDC experiments. The question is what would happen if the polarization during the TSDC experiment becomes “over-compensated” by the charge?

Such a situation arises when the heating gives place to cooling. During the subsequent cooling the polarization  $P$  is adjusting rapidly to the value of the charge  $\sigma$ . Thus, a part of the relaxed polarization is restored during the cooling to re-establish the equilibrium condition  $\sigma=P$ , so that the next cycle of the TSDC begins with the polarization equal to the charge at the end of the preceding cycle as shown schematically in Fig. 5.



**Fig. 5. Schematic diagram showing dynamic of the charge and the polarization during the fractional TSDC experiments.**

**PARTIAL RESTORATION OF POLARIZATION.** A part of the already relaxed residual polarization is restored after completion of the fractional heating. This is proven by the temperature dependence of the pyroelectric current measured during the cooling parts of the TSDC cycles. In the 2<sup>nd</sup> and 3<sup>rd</sup> cycles  $p$  increases during the cooling down to  $80^\circ\text{C}$  indicating an increasing polarization. The decrease of  $p$  at lower temperatures might be caused by thermal compression of the sample.

It appeared that the temperature of  $80^\circ\text{C}$  seems to be characteristic for PVDF, but the origin is not clear yet.

## CONCLUSION

1. The isothermal relaxation in short-circuited PVDF poled at room temperature is caused not by

the intrinsic conductivity, but rather by charge carriers injected during poling.

2. The dipole polarization in PVDF is less thermally stable than the compensating charge. However, a piece of the already relaxed polarization is restored during the cooling parts of the TSDC fractions in order to re-establish the equilibrium between the polarization and the charge.

3. In order to guarantee reversibility of the pyroelectricity, it is recommended to condition the poled PVDF samples by heating to 80 °C and cooling down.

4. The residual polarization and pyroelectricity irreversibly decrease if the poled PVDF is heated to higher temperature than that to which the sample was previously exposed.

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## ВЗАЄМОЗВ'ЯЗОК МІЖ ПІРОЕЛЕКТРИЧНИМИ ВЛАСТИВОСТЯМИ ТА ЗАЛИШКОВОЮ ПОЛЯРИЗАЦІЄЮ В ПОЛІВІНІЛІДЕНФТОРИДІ, ПРИЗНАЧЕНОМУ ДЛЯ ВИГОТОВЛЕННЯ ПІРОЕЛЕКТРИЧНИХ СЕНСОРІВ

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**Анотація.** Піроелектрика та фракційні термостимульовані струми деполяризації (ТСД) були експериментально вивчені в плівках полівініліденфториду (ПВДФ), електризованих шляхом застосування сильного постійного поля при кімнатній температурі. Отримана поляризація виявилась менш термічно стабільною, ніж корельований компенсуючий заряд. Дослідженням балансу заряду та піроелектричного коефіцієнта, виміряного під час охолодження у фракційному експерименті, показано, що захоплений компенсуючий поляризацію заряд відповідає за часткову перебудову поляризації під час охолодження.

Поляризація та об'ємні заряди у зразках ПВДФ, поляризованих застосуванням сильного поля при кімнатній температурі, не є термічно замороженими. Всі процеси їх зростання і релаксації взаємопов'язані. Якщо поляризація існує, то вона обов'язково компенсується захопленими зарядами.

Мета статті полягає в більш глибокому дослідженні природи залишкової поляризації в ПВДФ шляхом порівняння ТСД під час послідовного нагрівання поляризованих зразків до все вищих і вищих температур (фракційна ТСД) з піроелектричними струмами, отриманими під час подальшого охолодження зразка в кожному тепловому циклі.

Встановлено, що поляризовані зразки ПВДФ необхідно кондиціонувати шляхом нагрівання до 80 °C та охолодження для отримання стабільного пірокоефіцієнта.

**Ключові слова:** піроелектричні сенсори, ПВДФ, термостимульований струм деполяризації, сегнетоелектрики, поляризація.