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Influence of temperature conditions on thermostimulated depolarization of polyvinylidene fluoride films

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Abstract. The article investigates how the polarization temperature in the corona discharge field and pre-annealing modes of polyvinylidene fluoride copolymer films with tetrafluoroethylene effect thermally stimulated depolarization currents. The parameters of electrically active defects responsible for relaxation processes, the amount of charge (Q) released during depolarization and the value of the piezoelectric module d_{33} were determined for samples with different polarization temperatures. The article discusses the best temperature conditions for creating a piezoelectric state in polyvinylidene fluoride films.

Keywords: polyvinylidene fluoride, thermal activation spectroscopy, thermostimulated depolarization, corona discharge, electrically active defects

Introduction

Today, numerous fields of science and technology use a wide variety of devices. Many of them include dielectric materials made of polymer films. One of the promising materials in the field of electroactive polymers is polyvinylidene fluoride (PVDF) and its copolymer. PVDF is a piezoelectric polymer with unique properties lacking in traditional inorganic piezoelectrics, such as quartz or barium. The advantages of this material are high temperature stability during operation in the air, high rigidity at low temperatures, high mechanical strength, good electrical insulation, chemical and radiation resistance, and low flammability. These properties of polyvinylidene fluoride make the material suitable for use in various applications.

As of today, PVDF is the only polymer material with high piezoelectric properties. However, the technology of manufacturing piezoelectric elements from PVDF presents a few difficulties because high electric fields and elevated temperatures must be used in the polarization process (Shakirzyanov et al. 2016).

The paper investigates how polarization and pre-annealing temperatures impact the properties of PVDF-based piezoelectric elements during their manufacture. The paper also discusses optimal temperature parameters for polarization and pre-annealing of PVDF films.

Materials and methods

The study investigated F-2ME polyvinylidene fluoride (PVDF) films with a thickness of 20 microns and an orientation extraction coefficient of 3.5. The degree of crystallinity of the studied samples was approximately 55%, and the crystalline phase consisted mainly of the polar β-phase.

To create a piezoelectric state in the studied samples, polarization was applied in the corona discharge field at an elevated temperature ranging from 45 to 65 °C. The polarization time in the corona discharge field was 10 minutes, and the polarizing field was E = 1.2 MV/cm. During the polarization, the isometric state of the PVDF films under study was ensured.

The samples studied in the work were divided into three groups:

1) Without pre-annealing;
2) With pre-annealing at a temperature of 90°C in a free state for three hours;
3) With pre-annealing at a temperature of 90°C in an isometric state for three hours.

To study electrical relaxation in polymer materials, the method of thermally stimulated depolarization was used at the TSC II (France). The piezoelectric module d_{33} was determined using the YE2730A d_{33} Meter (USA).

Results

Fig. 1 shows TSD curves of PVDF samples that were pre-polarized at different Tp temperatures. It can be seen from the results that the maximum of the film depolarization current shifts to the high-temperature region with an increase in the polarization temperature of the samples.

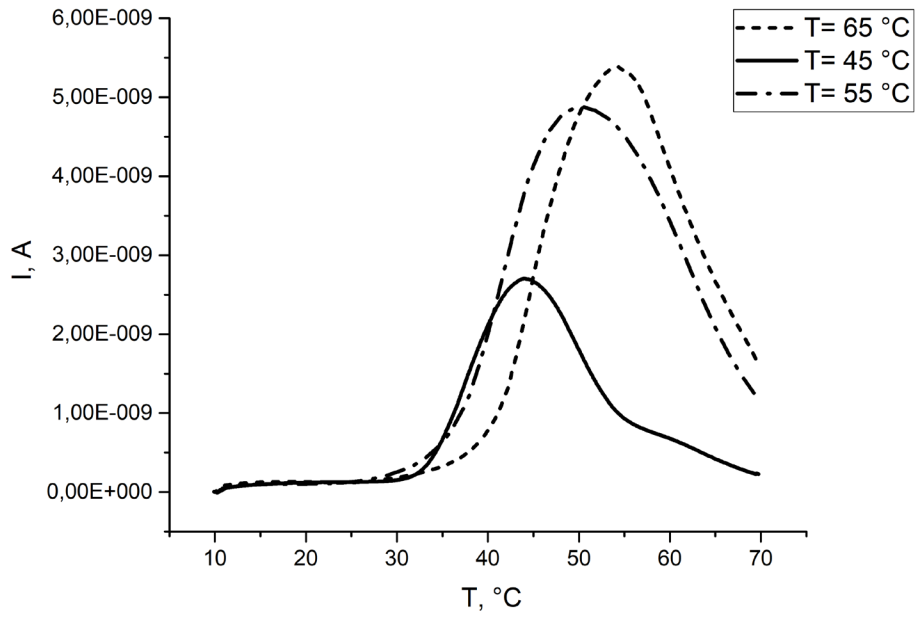

Fig. 1. TSD curves of PVDF samples with different polarization temperature Tp

According to (Butenko et al. 2008), the relaxation peak in this temperature region is associated with dipole relaxation in the crystalline phase or in regions intermediate between the crystalline and amorphous phases. The shift of the peak towards higher temperatures with an increase in the polarization temperature can be explained by the formation of more perfect and thermally more stable crystallites.

The activation energies of electrically active defects (EAD) responsible for this relaxation process were determined by the Garlick–Gibson method (Gorokhovatsky 1981) and are shown in Table 1.

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Table 1. Activation energies of EAD (Ea), the amount of charge released during depolarization (Q) and the value of the piezoelectric module d_{33} for different polarization temperatures of Tp samples

T_p, °C	E_a, eV	Q, C	d_{33}, pC/N
45	0.65 ± 0.02	$(9.37 \pm 0.01) \times 10^{-7}$	26 ± 1
55	0.76 ± 0.02	$(9.54 \pm 0.01) \times 10^{-7}$	30 ± 1
65	0.81 ± 0.02	$(9.72 \pm 0.01) \times 10^{-7}$	32 ± 1

As the polarization temperature increases, the area under the graph also increases and, consequently, the total number of relaxers that participate in the polarization process increases.

Thus, with an increase in the polarization temperature of PVDF films in the isometric state, the activation energy of electrically active defects and their number increases resulting in larger and more stable crystallites.

The mechanical relaxation of PVDF (Gorokhovatsky et al. 2020) developing in the same temperature region allows us to conclude that the electrical and mechanical properties of this material are closely interrelated. Mechanical stresses arising during heating can contribute to the formation of thermally stable crystalline regions in the polymer. This is confirmed by a slight increase in the piezoelectric module d_{33} of the studied samples observed with an increase in the polarization temperature with all other conditions being equal (Table 1).

From the above results, the optimal polarization temperature is Tp = 65°C. A further increase in temperature leads to numerous electrical breakdowns of the sample.

Figure 2 shows the results of thermally stimulated depolarization of samples with different heat treatments carried out before the polarization.

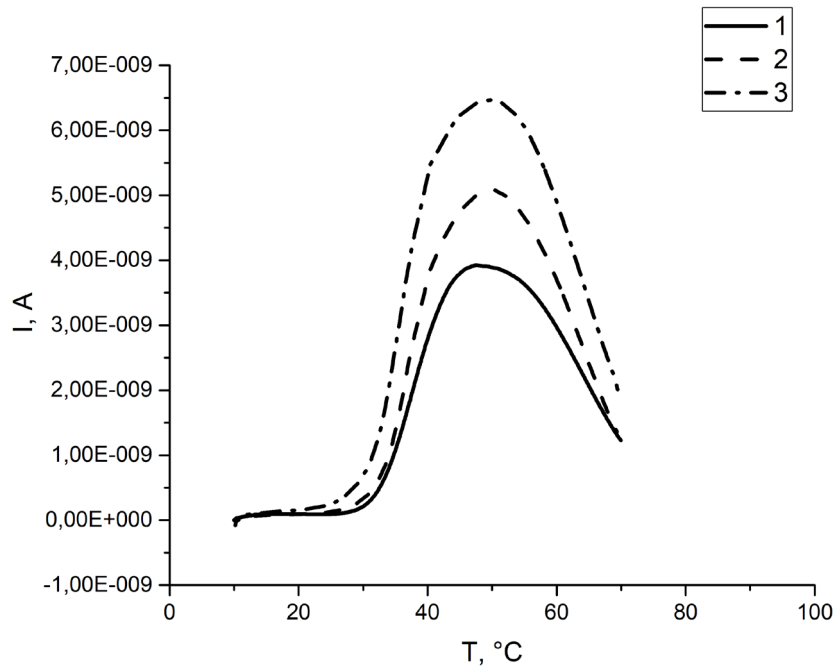

Fig. 2. TSD curves for PVDF samples polarized at Tp = 65° C with various preliminary temperature treatments: 1—without pre–annealing; 2—with pre-annealing in a non-isometric (free) state; 3—with pre-annealing in an isometric state

The position of the TSD peak does not depend on the conditions of heat treatment, however, the largest area under the curve is observed when isometric annealing is performed.

The obtained results show a pattern: PVDF samples pre-annealed in an isometric state have the largest area under the curve. This indicates that mechanical relaxation and polarization of PVDF are strongly interconnected.

Consequently, an increase in the time spent by the PVDF film in a mechanically stressed state (more than 3 hours for sample 3 and10 minutes for sample 1) leads to an increase in the number of crystallites involved in the polarization of samples.

Conclusions

The study of polarization and pre-annealing temperature regimes in PVDF films allows us to conclude that the retention of samples in an isometric state at an elevated temperature contributes to the improvement of their piezoelectric properties. This can be explained by the formation of more perfect crystallites during such annealing.

Preliminary annealing of samples in the isometric state at T = 90°C for 3 hours, followed by polarization at a temperature of Tp = 65°C in the corona discharge field, is the best temperature regime for creating a piezoelectric state in PVDF films.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took part in writing the article.

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