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The effect of ionizing radiation and etching time on low-temperature relaxation in polyvinylidene fluoride

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Abstract. This study examined the relaxation behavior of the semi-crystalline polymer polyvinylidene fluoride (PVDF) using the thermally stimulated depolarization (TSD) method. Experimental measurements were performed on thin PVDF films irradiated with heavy ions Ne^{4+} , Xe^{26+} , and Bi^{52+} with energies of about 1.2 MeV/nucleon for Ne^{4+} and Xe^{26+} , and about 3.1 MeV/nucleon for Bi^{52+} . Analysis of the obtained TSD spectra revealed the presence of three main relaxation processes at temperatures of around -45°C , 20°C and 40°C . The subsequent chemical etching of the films was found to lead to the emergence of a new relaxation process at a temperature of about -10°C , which may be due to the appearance of a new type of relaxers on the surface of the tracks.

Keywords: polyvinylidene fluoride, thermal activation spectroscopy, thermostimulated depolarization, track membranes, swift heavy ions (SHI)

Introduction

Polyvinylidene fluoride (PVDF) has gained widespread recognition in the field of micro-sensor and actuator development due to its outstanding mechanical, pyroelectric, ferroelectric and piezoelectric properties, as well as its exceptional biocompatibility (Kawai 1969; Pei et al. 2015). Thanks to these characteristics, PVDF films are actively used in the creation of skin sensors, implantable medical devices and microactuators (Ryu et al. 2005).

However, the performance of sensors and actuators based on PVDF can be significantly influenced by various types of radiation, such as ultraviolet, γ -rays, X-rays, low-energy ions and high-energy heavy ions. The interaction of these radiations with the polymer matrix of the sensor can alter various dielectric relaxation processes in PVDF.

Previous studies (Chailley et al. 1995) focusing on the behavior of PVDF under the influence of high-energy particles revealed that the degree of crystallinity of irradiated α -PVDF decreases depending on the

dose (or fluence) and the magnitude of the specific energy loss dE/dx of ionizing particles. A difference was noted between the rates of crystallinity loss for low-energy particles and high-energy ions. At low doses of irradiation with light particles, such as electrons, oxygen ions and neon ions, amorphization progresses more slowly compared to irradiation with heavier ions.

It is known that crystallinity is an important parameter that determines the piezoelectric, mechanical, optical, electrical and even thermal properties of polymers (Calcagno et al. 1994). However, the influence of high-energy heavy ions (SHI) on the dielectric relaxation properties of PVDF has been insufficiently studied. In polymers, charge accumulation and decay processes are primarily due to various dielectric relaxation processes, such as the orientation of permanent dipoles (orientational polarization), interfacial polarization and bulk charge polarization.

In this study, polyvinylidene fluoride (PVDF) films with a thickness of 9 μm were subjected to irradiation with various heavy ions, such as Ne^{4+} , Xe^{26+} and Bi^{52+} , with energies of approximately 1.2 MeV/nucleon for Ne and Xe and around 3.1 MeV/nucleon for Bi, as well as to etching with different exposure times. The fluence for each type of ion remained constant at approximately 10^9 cm^{-2} . At these specified energies, the ion ranges for Ne, Xe and Bi in PVDF are 13, 19 and 42 μm , respectively.

Thermally stimulated depolarization (TSD) current spectra were used for the analysis. TSD spectra provide a substantial amount of information about dielectric relaxation processes in the studied samples (Bhardwaj et al. 1983; Gorokhovatsky, Temnov 2007; Quamara et al. 2004; Sessler 1980).

Experimental results and discussion

The influence of ionizing radiation on relaxation processes in PVDF

Fig. 1 shows the TSD spectra of a thin polyvinylidene fluoride (PVDF) film irradiated with heavy ions Ne^{4+} , Xe^{26+} and Bi^{52+} , obtained under a polarizing electric field strength of 100 V/mm and a polarization temperature of 70 $^{\circ}\text{C}$.

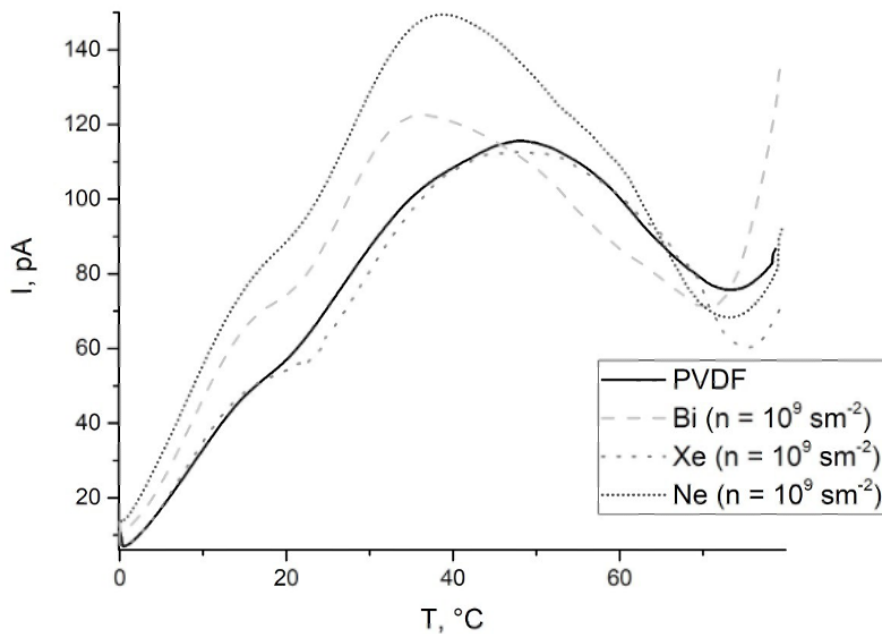


Fig. 1. TSD spectra for PVDF irradiated with heavy ions Ne^{4+} , Xe^{26+} and Bi^{52+} at a heating rate of 9 $^{\circ}\text{C}/\text{min}$ and a polarization temperature of 70 $^{\circ}\text{C}$

Within the temperature range of 0–60 $^{\circ}\text{C}$, two relaxation processes are observed, typically attributed to $\alpha\text{-C}$ -relaxation. This relaxation is associated with the dipole-segmental mobility that develops in the intermediate region between the amorphous and crystalline phases. The unfreezing of dipole mobility can occur near defects in the molecular chain (presumably around 20 $^{\circ}\text{C}$) as well as due to oscillations relative to the C-C chain in the crystalline phase of the polymer (presumably around 40 $^{\circ}\text{C}$) (Dmitriev et al. 2008).

Polarization of samples at 20 $^{\circ}\text{C}$ allows us to distinguish the relaxation process associated with defect formation within the volume of the polymer during its irradiation with ions of various types.

Fig. 2 shows the dielectric spectra (TSD spectra) for PVDF films obtained at a polarizing electric field intensity of 100 V/mm and a polarization temperature of 20 °C.

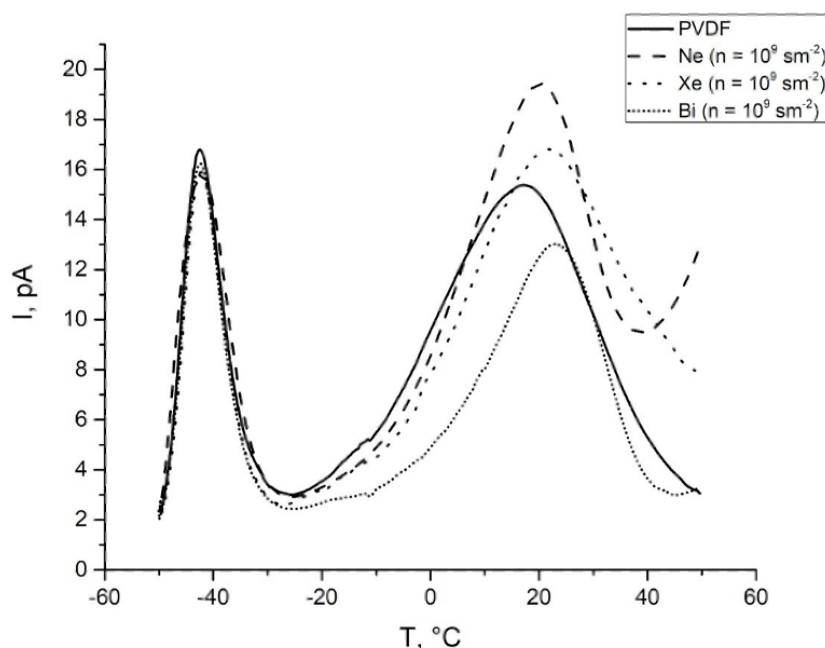


Fig. 2. TSD spectra for PVDF irradiated with heavy ions Ne⁴⁺, Xe²⁶⁺ and Bi⁵²⁺ at a heating rate of 9 °C/min and a polarization temperature of 20 °C

It is evident that the maximum of the relaxation process around 20 °C, under Bi ion irradiation, shifts towards higher temperatures, while the intensity of the corresponding TSD peak decreases compared to both the pristine polymer and polymers irradiated with Ne⁴⁺ or Xe²⁶⁺ ions. This indicates a reduction in the number of mobile molecular segments along with an impediment to their molecular mobility. Indeed, regardless of its crystalline phase, PVDF occupies an intermediate position between polymers that crosslink and those that degrade under irradiation. As the irradiation dose increases and approaches the so-called gel fraction D_g, which ranges from 10 to 35 kGy for PVDF, the dominant chain scission process begins to compete with the crosslinking process, ultimately leading to reduced mobility of molecular chains at lower irradiation doses.

In Fig. 3, the values of the activation energy of the relaxation process are presented as a function of ion charge, calculated using the method of varying the heating rate (Karulina et al. 2024). For irradiation with Bi ions, the activation energy is determined as 0.87 eV, which exceeds the activation energy of this relaxation process in the original unirradiated polymer by 0.2 eV.

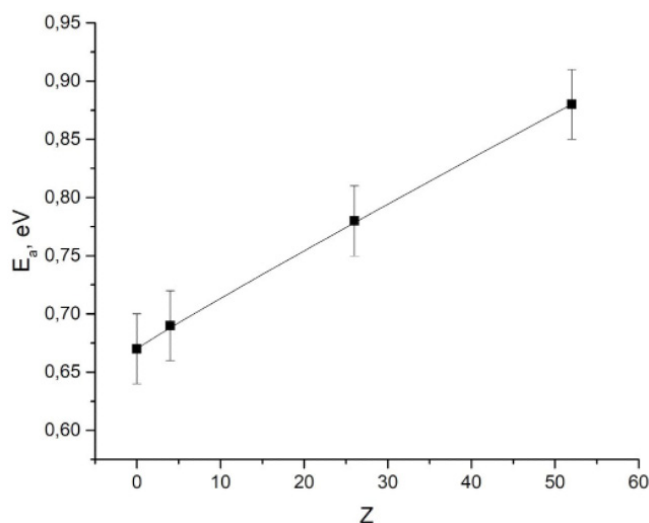


Fig. 3. Dependence of the activation energy on the charge of the incoming ion

The influence of etching on relaxation processes in PVDF

Fig. 4 shows the TSD spectra for PVDF films irradiated with Xe^{26+} ions and subjected to chemical etching for varying durations.

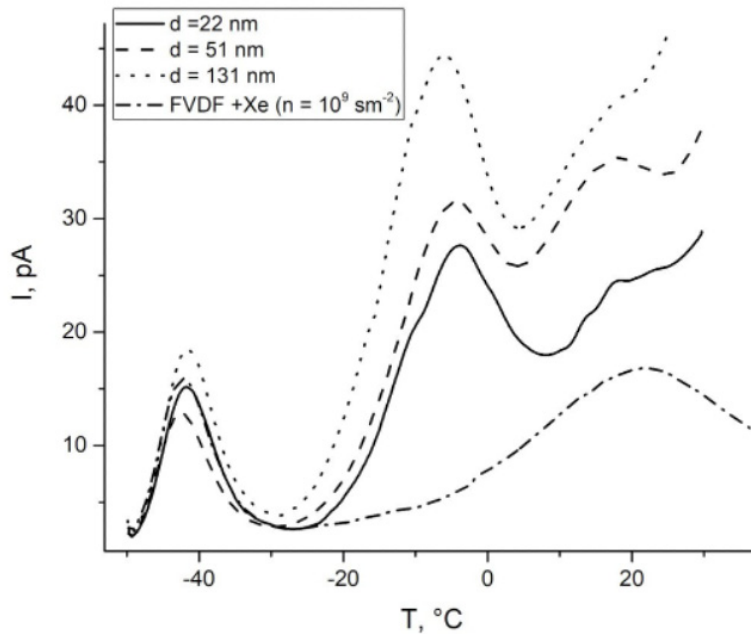


Fig. 4. TSD spectra for PVDF irradiated with heavy ions Xe^{26+} and subjected to etching of various durations at a heating rate of $9^\circ\text{C}/\text{min}$ and a polarization temperature of 20°C

Etching involves the penetration of small-sized etchant molecules into the core of ion tracks and selective cleavage of chemical bonds within the degraded core through chemical reactions (Apel, Fink 2004). This can lead to the formation of new relaxors in the vicinity of the track walls. In the TSD spectra, this manifests itself as the emergence of a new peak at around -10°C , absent in the films not subjected to etching. Its intensity increases with prolonged etching time, correlating with the increased surface area of tracks. The activation energy of this process, calculated using the method of varying the heating rate, was determined as 0.81 eV .

Conclusions

1. In the temperature range of $0\text{--}20^\circ\text{C}$, two relaxation processes were identified using the TSD method: α_1 at around 20°C (observed in both etched and non-etched irradiated films) and α_2 at around 10°C , observed only after etching.

2. Increased mass and energy of ionizing ions lead to reduced molecular mobility near forming molecular chain defects and a decrease in the number of mobile chain elements, consequently reducing the intensity of the TSD peak associated with the α_1 relaxation process. The activation energy of the α_1 relaxation process varies from 0.67 eV for the pristine polymer to 0.88 eV for the polymer irradiated with Bi ions.

3. The α_2 relaxation process is linked to the appearance of a new type of relaxors on the track surfaces resulting from chemical etching of the samples. Accordingly, its intensity increases with prolonged etching time. The activation energy of the α_2 relaxation process is 0.81 eV .

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.

References

- Apel, P. Y., Fink, D. (2004) Ion-track etching. In.: D. Fink (ed.). *Transport processes in ion-irradiated polymers. Springer Series in Materials Science*, vol. 65. Berlin, Heidelberg: Springer Publ, pp. 147–202. <https://doi.org/10.1007/978-3-662-10608-2> (In English)
- Bhardwaj, R. P., Quamara, J. K., Nagpaul, K. K., Sharma, B. L. (1983) Field-induced thermally stimulated currents in Kapton-H polyimide films. *Physica status solidi (a)*, 80 (2), 559–566. <https://doi.org/10.1002/pssa.2210800219> (In English)
- Calcagno, L., Musumeci, P., Percolla, R., Foti, G. (1994) Calorimetric measurements of MeV ion irradiated polyvinylidene fluoride. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 91 (1–4), 461–464. [https://doi.org/10.1016/0168-583X\(94\)96269-3](https://doi.org/10.1016/0168-583X(94)96269-3) (In English)
- Chailley, V., Balanzat, E., Dooryhee, E. (1995) Amorphization kinetics of poly (vinylidene fluoride) on high-energy ion irradiation. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 105 (1–4), 110–114. [https://doi.org/10.1016/0168-583X\(95\)00530-7](https://doi.org/10.1016/0168-583X(95)00530-7) (In English)
- Dmitriev, I. Yu., Gladchenko, S. V., Afanas'eva, N. V., et al. (2008) Molekulyarnaya podvizhnost' polivinilidenaftorida v anizotropnom sostoyanii [Molecular mobility of poly(vinylidene fluoride) in the anisotropic state]. *Vysokomolekulyarnye soedineniya. Seriya A*, 50 (3), 424–433. (In Russian)
- Gorokhovatski, Yu. A., Temnov, D. E. (2007) Termostimulirovannaya relaksatsiya poverkhnostnogo potentsiala i termostimulirovannye toki korotkogo zamykaniya v predvaritel'no zaryazhennom dielektrike. [Thermally stimulated relaxation of surface potential and thermally stimulated short circuit currents in the charged dielectric.] *Izvestiya Rossijskogo gosudarstvennogo pedagogicheskogo universiteta im. A. I. Gertsena — Izvestia: Herzen University Journal of Humanities & Sciences*, 8 (38), 24–34. (In Russian)
- Karulina, E. A., Volgina, E. A., Kulemina, S. M. et al. (2024) The effect of the montmorillonite-based filler on the electret properties of polypropylene. *Saint Petersburg State Polytechnical University Journal. Physics and Mathematics*, 17 (1), 29–37. <https://doi.org/10.18721/JPM.17103> (In English)
- Kawai, H. (1969) The Piezoelectricity of Poly(vinylidene fluoride). *Japanese Journal of Applied Physics*, 8, 975–983. <https://doi.org/10.1143/JJAP.8.975> (In English)
- Pei, S., Ai, F., Qu, S. (2015) Fabrication and biocompatibility of reduced graphene oxide/poly (vinylidene fluoride) composite membranes. *RSC Advances*, 5 (121), 99841–99847. <https://doi.org/10.1039/c5ra19228e> (In English)
- Quamara, J. K., Garg, M., Prabhavathi, T. (2004) Effect of high-energy heavy ion irradiation on dielectric relaxation behaviour of kapton-H polyimide. *Thin Solid Films*, 449 (1–2), 242–247. <https://doi.org/10.1016/j.tsf.2003.10.099> (In English)
- Ryu, J., Park, J., Kim, B., Park, J-O. (2005) Design and fabrication of a largely deformable sensorized polymer actuator. *Biosensors and Bioelectronics*, 21 (5), 822–826. <https://doi.org/10.1016/j.bios.2005.01.019> (In English)
- Sessler, G. M. (ed.). (1980) *Electrets*. Berlin: Springer Publ., 404 p. (In English)