Šiluminio ciklavimo įtaka feroelektriniam faziniam virsmui PVDF-TrFE pagrindu pagamintuose kompozituose: ultragarsinės spektroskopijos tyrimas

Effect of thermal cycling on ferroelectric phase transition of PVDF-TrFE based composites as investigated by ultrasonic spectroscopy

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Piezoelectric polymeric materials have a number of advantages in comparison with electroceramics, e.g., good mechanical flexibility, processability and robustness, lightness and the main one- low cost of production, whereas ceramics are brittle and difficult to process [1, 2]. Therefore, in this research work we focus our attention on copolymer of vinilidenefluoride and trifluoroethilene (PVDF-TrFE) based piezoelectric composites. P(VDF-TrFE) copolymer with a molar ration of 70/30 mol. % provides a reversible ferroelectric state with a high degree of crystallinity (more than 80 %) that is responsible for its strong electromechanical properties [1, 3-7].

In this paper we report on the investigation of ultrasonic wave attenuation, velocity and ultrasonically induced piezoelectric voltage in P(VDF-TrFE) composites with fillers of conductive carbon nanotubes (CNT). Measurements have been carried out over a temperature range from 300 K to 390 K using ultrasonic automatic pulse-echo method.

The temperature dependencies of ultrasonic velocity and attenuation showed anomalies attributed to Curie temperature T_c and a structural relaxation also known as β - relaxation process. Large thermal hystereses have been observed in both temperature dependences of ultrasonic velocity and piezovoltage. Moreover, temperature dependences of ultrasonic velocity and attenuation were shown to be sensitive to thermal cycling over ferroelectric transition (Fig. 1).

The existence of the shoulder in the ultrasonic loss curve may be explained by the proposed elsewhere [8-10] existence of a crystalline intermediate γ phase or a recrystallization of an anchored amorphous phase and thus a change of the amount of the imperfect crystallites on cooling after it was annealed near T_m. Our measurements have confirmed results observed by [8-10] when the shoulder disappears in beforehand annealed samples. As seen from Figure 1 the shoulder observed on heating (Fig. 1a) vanishes after the sample was annealed near 415 K (Fig. 1b).

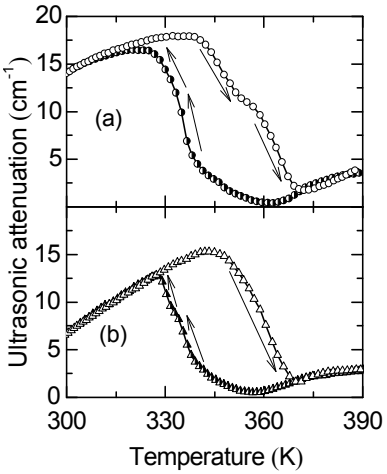

Fig. 1. Temperature dependences of the ultrasonic attenuation in 1 vol. % P(VDF-TrFE)/CNT composite (a) before and (b) after annealing near 415 K. Arrows show direction of temperature variation

Keywords: Annealing, thermal cycling, P(VDF-TrFE)

References

[1] T. R. Dargaville, M. C. Celina, J. M. Elliott, P. M. Chaplya, G. D. Jones, D. M. Mowery, R. A. Assink, R. L. Clough and J. W. Martin, *Characterization, Performance and Optimization of PVDF as a Piezoelectric Film for Advanced Space Mirror Concepts* (Sandia National Laboratories, United States, 2005).
[2] M. V. Silibin A. V. Solnyshkin, D. A. Kiselev, A. N. Morozovska, E. A. Eliseev, S. A. Gavrilov, M. D. Malinkovich, D. C. Lupascu and V. V. Shvartsman, Journal of Applied Physics, J. Appl. Phys. **114**, 144102 (2013).
[3] T. Furukawa, Ferroelectric properties of vinylidene fluoride copolymers, Phase Transitions, 18, 143-211 (1989).
[4] K. Tashiro, *Crystal structure and phase transition of PVDF and related copolymers* (Ferroelectric polymers, New York 1995).
[5] R. A. Pethrick, *The applications of ferroelectric polymers* (Applications of ferroelectric polymers, Glasgow, 1988).
[6] H. Kawai, Japanese Journal of Applied Physics, **8**, 975 (1969).
[7] J. F. Legrand, J. Lajzerowicz, B. Berge, P. Delzenne, F. Macchi, C. Bourgaux-Leonard, A. Wicker and J. K. Kruger, Ferroelectrics, **78**, 151 (1988).
[8] R. L. Moreira, P. Saint-Gregoire, M. Lopez and M. Latour, Journal of Polymer Science: Part B: Polymer Physics, **27**,709 (1989).
[9] R. L. Moreira, P. Saint-Gregoire and M. Latour, Phase Transitions, **14**, 243 (1989).
[10] R. L. Moreira, R. Almairac and M. Latour, J. Phys.: Condens. Matter, **l**, 4273 (1989).