Abstract: The thermal stability of piezoelectric d₃₃ coefficients and charge dynamics in the piezoelectret films with tailored microstructure, made of non-porous polytetrafluoroethylene (PTFE) and fluoroethylenepropylene (FEP) layers, are of the isothermal decay investigated by the measurements of piezoelectric d_{33} coefficients at elevated temperatures and the analysis of thermally stimulated discharge (TSD) current spectra in short circuit, respectively. The results show that the quasi-static piezoelectric d₃₃ coefficient up to 300 pC/N is achieved and its Young's modulus is about 0.28 MPa. The d₃₃ values in the present studied films show improved thermal stability compared with the films without regular microstructure. The drift path for the most of detrapped charges in the films is through the solid dielectric layer