EDN: NWLQBE

УДК 666.655; 621.315.612 *2.2.6*

PIEZOELECTRIC ENHANCEMENT IN P(VDF-TRFE) COPOLYMER FILMS BY CONTROLLED CRYSTALLIZATION

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Absrtact. The rapid advancement of wearable electronics and the Internet of Things necessitates the development of flexible sensors capable of accurately detecting physical and chemical signals. Piezoelectric polymers, specifically Poly(vinylidene fluoride)-trifluoroethylene [P(VDF-TrFE)] copolymers, are promising materials for these applications due to their flexibility and electroactive properties. However, their relatively low piezoelectric coefficients limit sensitivity. This study investigates the enhancement of piezoelectric performance in P(VDF-TrFE) films through controlled crystallization induced by polytetrafluoroethylene (PTFE) templates. The anisotropic crystallization behavior significantly improves the films' crystallinity, ferroelectric properties, and piezoelectric coefficients, as confirmed by AFM, XRD, and nanoscale analyses. The templated films exhibit stronger piezoelectric responses, including improved d33 coefficients and directional piezoelectric anisotropy, enabling more sensitive mechanical excitation detection in flexible devices. These findings highlight templating-guided crystallization as a viable strategy for optimizing the performance of piezoelectric polymers in next-generation flexible sensors.

Keywords: Piezoelectric polymers, P(VDF-TrFE), Controlled crystallization, PTFE template, Flexible sensors, Ferroelectric properties, Wearable electronics.

The vigorous development of wearable electronics and the Internet of Things greatly depends on design and development of flexible sensors, which effectively perceive both physical and chemical signals from human bodies and the surroundings. Contact perception is especially concerned and usually realized based on piezo-capacitive, piezo-resistive, piezo-electric, and even tribo-electric effects. Piezoelectric materials can convert mechanical excitation into electrical response via electrostatic interaction between electrodes and dipoles inside piezoelectric film and are widely utilized to construct self-powered stress/strain sensors. Inorganic piezoelectric ceramics and crystals are mostly used due to their high piezoelectric performance. However, intrinsic brittleness and hardness limit their applications in flexible sensors. As comparison, piezoelectric polymers, such as Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene P(VDF-TrFE), attract more and more attention for flexible electronics though their relatively lower piezoelectric coefficients, for example d_{33} value of -25 pC/N much lower than those of several hundreds of pC/N from inorganic piezoelectrics, greatly degrade their sensitivity to weak mechanical excitation. Modulation of microstructures and crystallinity is a feasible route to promote electroactivity of piezoelectric polymers, in which templating guidance measure is especially effective and convenient. Textured P(VDF-TrFE) films were grown on graphene/copper surfaces, which was attributed to a pattern potential that originated from charge transfer between the graphene and Cu surface[1]. Our previous work also verified that on polytetrafluoroethylene (PTFE) templates, P(VDF-TrFE) films presented anisotropic crystallization behaviour with well improved crystallinity and electroactivities. In this report I will introduce the work on PTFE template induced crystallization and its influence on electroactive behaviour of piezoelectric copolymer films.

PTFE templates were fabricated via friction transfer technique, which presented parallel nanogroove structure (Figure 1a). Then P(VDF-TrFE) films were spin coated onto the PTFE layers and annealed at a temperature above melting point (~150 ^oC) of P(VDF-TrFE). PTFE-induce copolymer films presented long and parallel stripe-like crystallites (Figure 1b). As comparison, the control sample without PTFE templating only presented disordered and needle-like crystallites (Figure 1c). Varied-XRD analysis indicated that these PTFE-induced copolymer films still followed the first-order phase transition (Figure 1d). Nanoscale thermal analyses further verified that the anisotropically crystallized film showed relatively higher melting point than that of the control film (Figure 1e). polarization-electric field hysteresis loops exhibited enhanced remanent polarization of PTFE-induced films (Figure 1f). In our current technology, PTFE templates can induce anisotropic crystallization of P(VDF-TrFE) films with thickness up to about 10 um.

Via home-made d_{33} measurement system (Figure 2a), we conducted piezoelectric characterization of PTFE-induced copolymer films. At driving frequency range between 50 Hz and 800 Hz, PTFE-induced device presented an averaged d_{33} value of -40.7 pC/N, about 61% enhancement to that of copolymer film without PTFE templating (Figure 2b). Furthermore, anisotropically crystallized P(VDF-TrFE) device showed in-plane anisotropic piezoelectric performance (Figure 2c). This device with high sensitivity to weak mechanical signals can be used for detection of physiological activities, such as pulsation (Figure 2d).

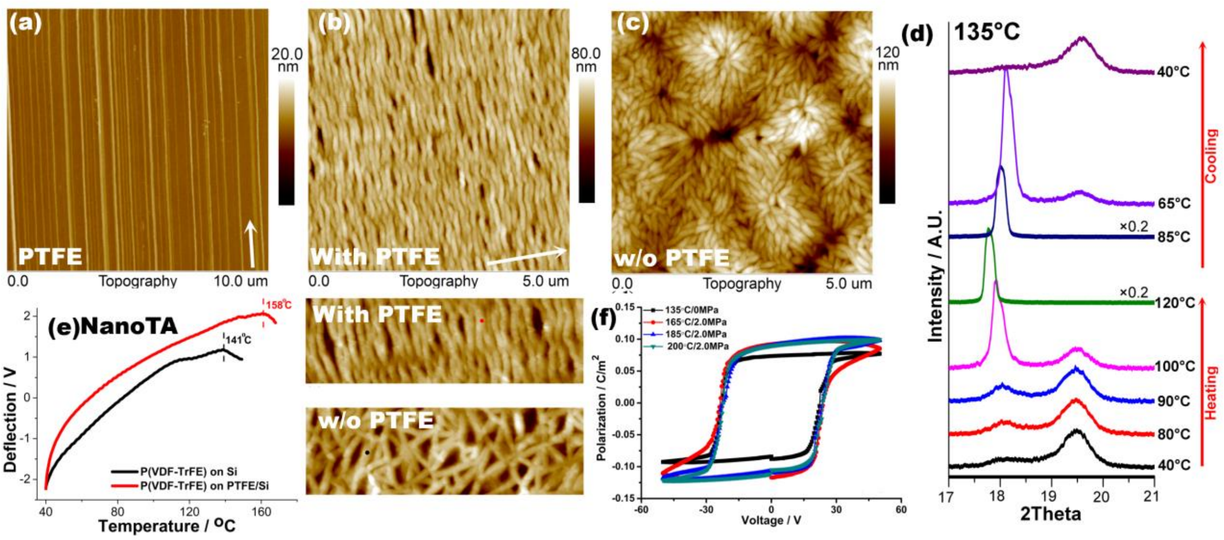

Figure 1. PTFE-induced anisotropic crystallization of P(VDF-TrFE) films[2, 3].
AFM morphology of (a) PTFE template, P(VDF-TrFE) (b) with and (c) without PTFE templates. (d) Varied-temperature XRD analysis of PTFE-induced copolymer film. (e) Nanoscale analyses of copolymer films with and without PTFE templates.
(f) Ferroelectric performance

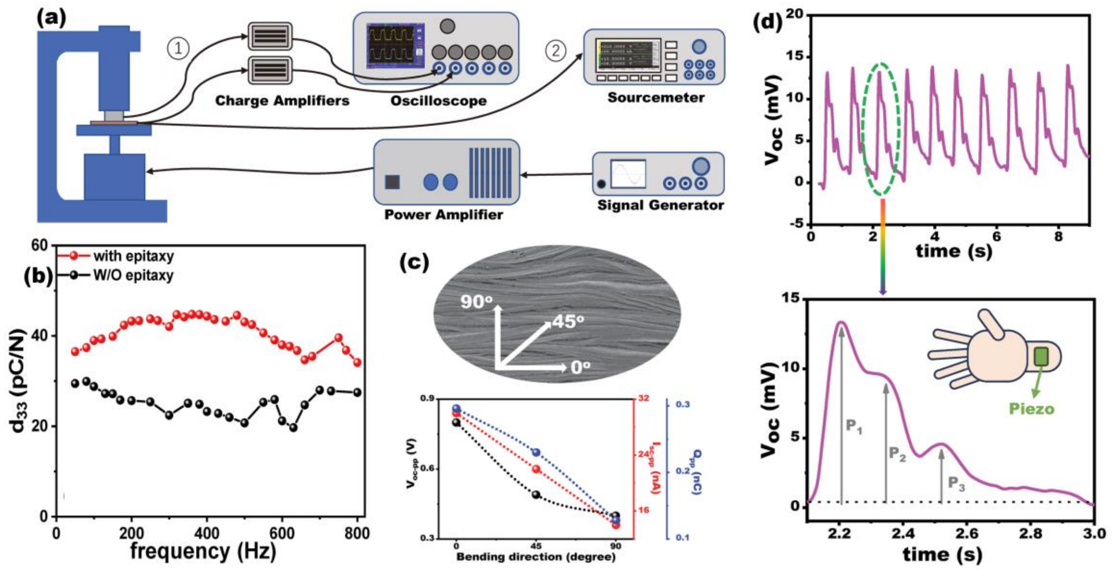

Figure 2. Piezoelectric performance of PTFE-induced copolymer films[4, 5]. (a) Schematic of the d_{33} measurement system. (b) d33 coefficient values at different driving frequency from both copolymer films with and without PTFE templating. (c) in-plane anisotropic piezoelectric response. (d) pulsation detection of a volunteer.

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ПЬЕЗОЭЛЕКТРИЧЕСКОЕ УСИЛЕНИЕ В СОПОЛИМЕРНЫХ ПЛЕНКАХ P(VDF-TRFE) ПУТЕМ УПРАВЛЯЕМОЙ КРИСТАЛЛИЗАЦИИ

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Аннотация. Стремительное развитие носимой электроники и Интернета вещей диктует необходимость разработки гибких датчиков, способных точно обнаруживать физические и химические сигналы. Пьезоэлектрические полимеры, в частности сополимеры поливинилиденфторида и трифторэтилена [P(VDF-TrFE)], являются перспективными материалами для этих приложений благодаря своей гибкости и электроактивным свойствам. Однако их относительно низкие пьезоэлектрические коэффициенты ограничивают чувствительность. В данном исследовании изучается улучшение пьезоэлектрических характеристик пленок P(VDF-TrFE) посредством контролируемой кристаллизации, индуцированной шаблонами из политетрафторэтилена (ПТФЭ). Анизотропное поведение кристаллизации значительно улучшает кристалличность, сегнетоэлектрические свойства и пьезоэлектрические коэффициенты пленок, что подтверждено анализами АСМ, рентгеновской дифракции и наномасштабными исследованиями. Шаблонные пленки демонстрируют более сильные пьезоэлектрические отклики, включая улучшенные коэффициенты d33 и направленную пьезоэлектрическую анизотропию, что позволяет более чувствительно обнаруживать механическое возбуждение в гибких устройствах. Эти результаты показывают, что кристаллизация с использованием темплатов является перспективной стратегией оптимизации характеристик пьезоэлектрических полимеров в гибких датчиках нового поколения.

Ключевые слова: Пьезоэлектрические полимеры, P(VDF-TrFE), Управляемая кристаллизация, шаблон из ПТФЭ, Гибкие датчики, Сегнетоэлектрические свойства, Носимая электроника\

Материалы представлены на Международной научно-практической конференции «Современные подходы и практические инициативы в инженерных науках» (г. Казань, 2-3 октября 2025 года).

Статья представлена в редакцию 15 августа 2025 г.