

ACHIEVING SYNERGISTIC IMPROVEMENT IN DIELECTRIC AND ELECTROCALORIC EFFECT OF ALL-ORGANIC FERROELECTRIC POLYMER NANOCOMPOSITES

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Abstract

Electrocaloric effect based refrigeration is an innovative zero global warming potential (GWP) thermal management technology. Polyvinylidene fluoride (PVDF) and its copolymers/terpolymers possess advantageous properties such as lightweight, flexibility and easy processability, and have found extensive applications in sensing, transducing and energy applications. In this study, we found that an optimal loading of low-permittivity organic small molecular 3,3-diphenyl acrylonitrile (DPA) into the P(VDF-TrFE-CFE) terpolymer matrices substantially improves the polarization efficiency and the dielectric characteristics. The blend intermolecular interface with large dielectric difference enabling the polar phases within the polymer to adopt a state of reduced energy barrier for electric-field-induced switching. As a result, the ferroelectric polymer nanocomposites modified by DPA molecular exhibits over 150% entropy change enhancement over the based terpolymer under the same field strength. The present work leverages the interfacial coupling mechanism as a strategy to develop high-performance electrocaloric composites for solid-state refrigeration applications.

Keywords: *All-trans* conformation; Electrocaloric effect; Nanocomposite; Terpolymer

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Introduction

The electrocaloric effect (ECE) has garnered considerable attention in recent decades due to its prospective utility in eco-friendly, high-efficiency solid-state refrigeration. This effect engenders a reversible shift in electric dipole entropy via the cyclical polarization and depolarization of a solid dielectric substance (Shi *et al.*, 2019). The application or withdrawal of an external electric field can induce an adiabatic temperature shift (ΔT) or an isothermal entropy variation (ΔS) within dielectric substances. Materials such as inorganic ferroelectrics (inclusive of single crystals and bulk ceramics), ferroelectric polymers, and their composites are at the forefront of ECE cooling. This is attributed to their inherent polarization, which can be directed by an external electric field (Ali *et al.*, 2022). Among all the EC materials, PVDF-based polymers are particularly promising for solid-state cooling applications. Their appeal lies in their unique characteristics, which include flexibility, scalability, biocompatibility, and cost-effectiveness (Qian *et al.*, 2023).

Considering the low thermal conductivity and the inevitably persistent ferroelectric loss especially at high fields for the neat EC polymers, recent research has turned to a composite approach. This method combines the complementary properties of inorganic ferroelectric ceramics and relaxor organic polymers to enhance overall electrocaloric performance (Shi *et al.*, 2019). A variety of ferroelectric ceramic nanoparticles have been incorporated into the polymer matrix due to their high dielectric constant, high thermal conductivity, and electrical insulation properties, contributing to the development of polymeric electrocaloric nanocomposites (Cai *et al.*, 2023).

However, the compound inorganic oxide will also introduce some unfavourable factors to the polymer system for the completely different physical and chemical properties between inorganic and organic matters. Most of the reported nanocomposite works, both two composites were combined to form a film by simple blending, which will cause inhomogeneity and discontinuity of inorganic-organic interfaces (Qian *et al.*, 2019). The poor dispersibility of inorganic nanoparticles in the organic system often results in agglomeration during film formation, compromising the repeatability of film preparation due to agglomeration, holes, and cracks. Consequently, this can lead to a reduction in breakdown strength, an increase in dielectric loss, and an increase in interface defects (Zhang *et al.*, 2015).

To circumvent the irreversible issues associated with inorganic nanoparticles, an organic nanoparticle-polymer composite system can be considered. However, research on all-organic electrocaloric nanocomposites is limited, with the exception of incorporating graphene into terpolymers (Yang *et al.*, 2016), while normal high voltages cannot be applied due to the transport of free electrons within the graphene layer. There are few research studies have focused on all-organic composite EC films by incorporating organic small molecules into the PVDF-based polymer matrix. Therefore, there is a pressing need to develop high-performance electrocaloric nanocomposites with more *all-trans* conformations through the intermolecular interaction between small molecules and PVDF polymers.

In this study, we incorporated unconventional 3,3-diphenyl acrylonitrile (DPA) small organic molecular into the P(VDF-TrFE-CFE) terpolymer matrices, the low-permittivity DPA molecular were extensively incorporated in the non-polar polymer dielectrics and establishes intermolecular interaction with the polymer chains, and enhanced net spontaneous polarization of the all-organic composites (Su *et al.*, 2022). As a result, with a low content of DPA in the ferroelectric polymer, we observed a starkly distinguished phenomenon that the dielectric constant of 60 and 150% EC entropy change enhancement compared to the base terpolymer.

Experimental

Materials

The terpolymer P(VDF-TrFE-CFE) with a composition of VDF/TrFE/CFE = 65/35/7 mol% was supplied by Piezo Technologies of Arkema, France. The 3,3-diphenyl acrylonitrile (DPA, 97%, RG) was purchased from Adamas. And *N*, *N*-dimethylformamide (DMF, 99.8%+, HPLC) was provided by Sigma-Aldrich.

Preparation of the PVDF/DPA Composite Films

The resulting films were obtained via solution casting with a typical thickness of about 10-15 μm . The terpolymer was dissolved in *N*, *N*-dimethylformamide solvent at a concentration of 2 wt%, the DPA solution (DPA powder was dissolved in DMF with a concentration of 100 mg mL⁻¹) was added according to the 0.5%-5% mass concentration ratio. After mixing the mixture

thoroughly stirred, the solution was dropped onto a clean quartz plate substrate and dried at 60°C for 8 h. Subsequently, the films were peeled off from the plates and vacuum annealed at 120°C overnight, then slowly cooled to room temperature.

Characterization

^1H -NMR spectra were recorded on a Bruker Advance III 600 MHz spectrometer, and all the samples were prepared in deuterated dimethylsulfoxide (d_6). Transmission electron microscopy (TEM) image were obtained on FEI Talos F200X electron microscopy. Fourier transform infrared spectroscopy (FTIR) measurement was characterized using Nicolet 6,700 in the attenuated total reflectance (ATR) mode using 4 cm^{-1} of resolution and 32 scan times. The differential scanning calorimetry (DSC) analysis was conducted on a TA Instrument (TA-DSD25) in nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) were performed at the BL19U2 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 0.124 nm. Young's modulus was derived from strain-stress curve carried out on a ZQ-990LA-2 stretcher using a 10-N load cell and an extension rate of 20 mm min^{-1} .

Dielectric spectroscopy was acquired with Broadband Turnkey Dielectric Spectroscopy system (PolyK) and multi-frequency LCR meter (HP 4284A), in conjunction with a digitally controlled chamber (EC1A Test Environment

Chamber, Sun Electronics) and nitrogen tank. The polarization-electric field (P - E) polar loop was measured with Ferroelectric Polarization Loop and Dielectric Breakdown test system (PolyK) with 609C-6 trek.

Results and Discussion

Characterization of the All-organic Nanocomposites

The aim of this work is to investigate the influence of the intermolecular interaction on the dielectric behaviour and electrocaloric effect of all-organic ferroelectric PVDF-based nanocomposites. DPA molecular was introduced as a nucleating agent with low-permittivity to promote the polarization efficiency and dielectric characteristics, which can maximize and maintain the zigzag alignment of $-\text{CF}_2$ and $-\text{CH}_2$ groups within the terpolymer chains at the large dielectric difference interface (Su *et al.*, 2022). As a result, the homogeneous composite film with 2% gravimetric content of DPA was transparent and colourless without aggregation or holes as shown in Figure 1(a).

The results of the nuclear magnetic hydrogen spectrum revealed that the intermolecular interaction between the DPA and PVDF reduces the extranuclear electron cloud density of the active hydrogen atoms near the cyan group on the DPA framework. This results in the chemical potential moving to the lower field. The intrinsic chemical

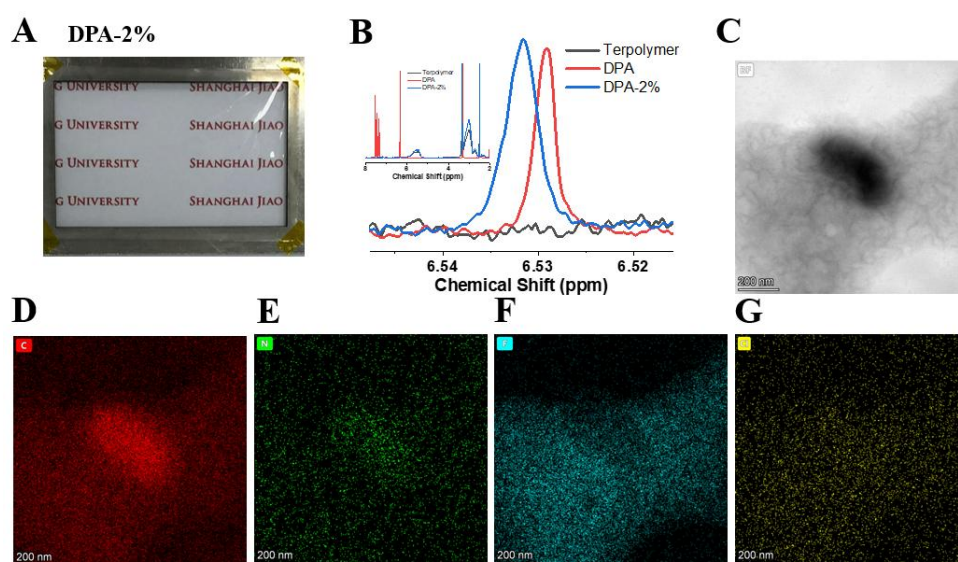


Figure 1. (A) The prepared film of DPA-2%. (B) The ^1H -NMR (DMSO-d_6) of pure DPA small molecular, terpolymer and DPA-2% nanocomposite. (C) The TEM image and (D-G) EDS elemental mapping images of C, N, F, and Cl in the selected area

shift of DPA was about 6.528, while it increased to about 6.534 when the terpolymer substrate was doped with 2% gravimetric content of DPA (denoted as DPA-2%) as shown in Figure 1(b).

Transmission electron microscopy (TEM) and elemental mapping images of C, N, F, and Cl on the DPA nanocomposites were illustrated in Figure 1(c-g). The presence of DPA small molecules can be determined by the distribution of carbon and nitrogen elements. The DPA nanoparticle was completely enveloped by the terpolymer matrix, there was no significant solid-solid phase separation around the boundary from the fluorine and chlorine elemental mapping images, indicating the existence of the intermolecular interaction with large polarity difference.

The Crystal Structure Analysis on the Effects of DPA on Terpolymer

This study seeks to evaluate the influence of DPA crystals within the terpolymer. To this end, we performed several structural analyses on TP and a series of DPA samples. Fourier transform infrared spectroscopy (FTIR) of the bared terpolymer and modified nanocomposites with varying DPA contents (0.5%-5%) are depicted in Figure 2(a). The absorption peaks of the polar crystal region were mainly at 840 and 1,280 cm^{-1} (the inset of Figure 1(a), and the addition of organic small

molecules have promotion for the formation of polar-crystals during the crystallization of terpolymer. The FTIR result can validate the role and functionality of the interface interaction in the terms of arrangement and orientation of the PVDF chains toward *all-trans* conformation, which may further promote the net spontaneous polarization and electrocaloric of the fluoropolymer nanocomposites.

The latent heat in the crystallinity of the base terpolymer and 0.5%-5% DPA nanocomposites were measured via differential scanning calorimetry (DSC) measurement. Both samples were initially cooled to -50°C and then subjected to two cycles of heating and cooling between -50°C and 150°C at a ramp rate of $10^{\circ}\text{C}/\text{min}$. The first heating tests for these EC materials are shown in Figure 2(b), and Figure 2(c) is the second cooling DSC data to eliminate the effect of thermal history. A distinct peak for the polar-nonpolar transitions shifted from 30°C to 35°C once DPA was incorporated into the polymer, and the peak became increasingly pronounced with the addition of DPA, indicating a lower phase transition barrier. The increased transition temperatures after incorporating small molecules also indicated the formation of the interfacial polarization.

The melting enthalpy of TP was 21.1 J/g, compared to 22.1 J/g for DPA-1%, 23.1 J/g for DPA-2%, and 23.0 J/g for DPA-5% (Figure 2(b)),

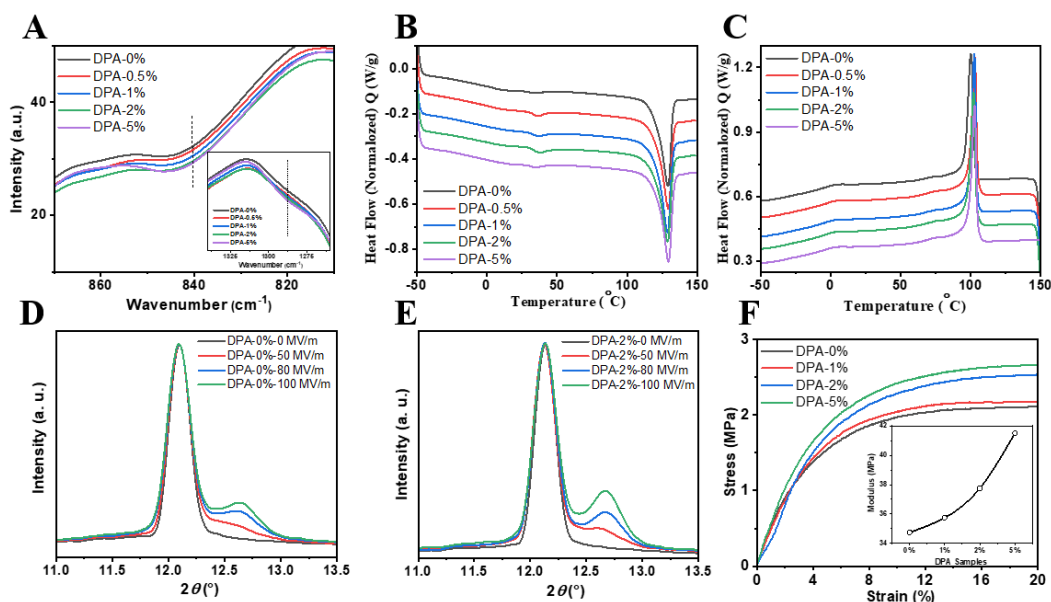


Figure 2. (A) The FI-TR spectres of different DPA composite films at the polar phase wavenumber of 840 and 1,280 cm^{-1} . (B) DSC of the first heating thermograms, (C) DSC of the secondly cooling thermograms. (D) In-situ WAXD patterns of base terpolymer, and (E) DPA-2% samples under 0 to 100 MV/m. (F) Young's modulus of the different DPA nanocomposites films

DPA-2% has the largest enthalpy change by comparison. The second cooling progress was also showed a similar improvement in crystallization enthalpy (Figure 2(c)) and in WAXD without applied electric field at (Figure 2(d-e)). The enhancement of crystallinity in the nanocomposite polymer was obviously, suggesting that the small DPA fillers introduce a dramatically increased are of the heterogeneous interface, and most of the emerged polar entities were generate at the interfaces between DPA molecular and terpolymer.

To verify the origin of the colossal ECE for this all-organic system, we conducted *in-situ* WAXD to investigate the dynamic transition of the interfacial crystalline structures under electric fields (Figure 2(d-e)). The presence of 2% DPA crystals in polymer substrates stimulated a strong phase transition compared to the neat TP and the field-induced polar fraction of bulk domains increased to 34% when the electric field was increased to 100 MV/m, while for the base terpolymer only 20% was converted. Hence, the established interfacial interaction between DPA and $-CF_2$ moieties on PVDF could be responsible for the induced interfacial *all-trans* configuration driven by electric fields (Qian *et al.*, 2021). The low-permittivity DPA molecular could reduce the energy barrier of phase transition under electric field, which would further work with the enhanced polar randomness to further enhance the ECE.

As the proportion of DPA crystals added to the polymer substrate increased, the mechanical properties of the composite films also improved. Figure 2F exhibits the in-plan strengthened Young's modulus (Y) of the DPA modified samples, enhanced Y over the pure terpolymer are observed for all the nanocomposites (from 34.4 to 41.5 MPa), and the higher Young's modulus of the DPA films lead to higher resistance to electromechanical breakdown, which is conducive to the long-term

stable operation of practical industrial refrigeration devices in the future.

Dielectric Analysis and EC Enhancement

The temperature-dependent permittivity revealed an outstanding feature as the terpolymer is being converted to the modified series with increasing DPA contents as shown in Figure 3(a). The pristine permittivity peak of relaxor terpolymer at about 20°C showed the formation of the spontaneously polarized phases. The addition of the low permittivity DPA crystals significantly suggested the low-field dielectric constant and decreased the dielectric loss in the DPA modified systems by the large dielectric difference and intermolecular interaction around the interfacial. And a more prominent second peak at about 38°C indicating the highly localized polar entities with stronger interfacial polar phase.

The permittivity increased with the introduction of DPA crystals and the largest dielectric constant of DPA-2% was nearly 60, which was about 30% higher than the base terpolymer, while it decreased when the DPA content is further increased to 5%. The counterintuitive pinning effect at about 38°C of DPA samples suggested that the DPA induced interface defects prevent the formation of bulky and strongly correlated polar regions, which were especially valuable considering that the overall crystallinity is increasing as mentioned by DSC and WAXD results.

The corrected bipolar polarization-electric field loops of the blank polymer and nanocomposites under 100 MV/m at 10 Hz and room temperature were given in Figure 3(b). The maximum polarization of the PVDF-based nanocomposites clearly increased with increased DPA filler loading. DPA-2% exhibited an induced polarization of 0.066 C/m² higher for terpolymer of 0.05 C/m² under the high electric field of

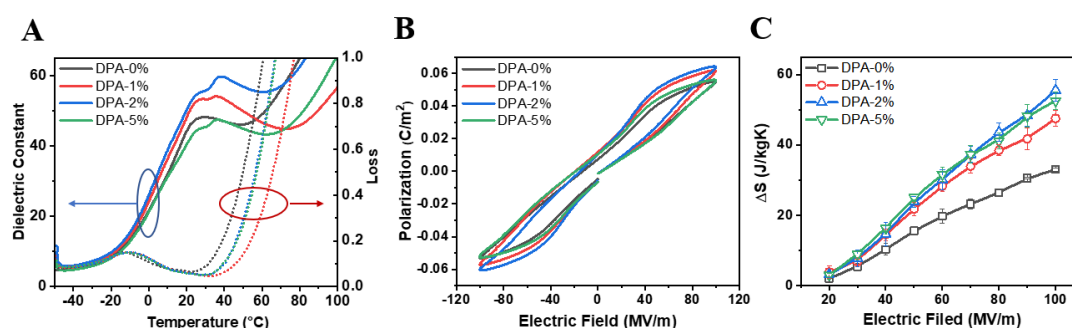


Figure 3. (A) Temperature dependent dielectric constant and loss of series DPA samples at 100 Hz. (B) Polarization loop of series DPA samples at 10 Hz and 100 MV/m. (C) ECE results of series DPA samples from 20 to 100 MV/m

100 MV/m, which was consistent with the changing trend of the temperature-dependent dielectric constant. However, when the content of the organic small molecule crystal reaches 5%, more space charge and defect loss may be introduced due to agglomeration and resulting in decreased polarization.

The dielectric performances of the films are closely related to the electrocaloric effect performances. We were surprised to find that the DPA-modified terpolymer (DPA-2%) exhibited a markedly improved electrocaloric effect. We observed an entropy change of nearly 55 J/kg·K under 100 MV/m, which corresponds to an adiabatic temperature change about 11 K as shown in Figure 3(c). It is also evident that the enhancements in ECE is more pronounced at high operating electric fields, where the stronger electric-potential further attracts PVDF chains to crystallize on DPA interface in polar phase arrangement and expedites the transformation of local amorphous regions into the polar crystalline phase by the interface dielectric difference effect.

Conclusions

In summary, a high-performance dielectric and electrocaloric effect composite was fabricated via counter-intuitively including a low-permittivity organic small molecular nano-insulator. We have discovered that introducing organic small molecular 3,3-diphenyl acrylonitrile (DPA) into PVDF-based terpolymer matrices will significantly enhances the polar-phase ratio. DPA establishes a strong interface effect with terpolymer to reducing the energy barrier from nonpolar-phase to polar-phase transformation confirmed by series structure and dielectric analysis. Consequently, the ferroelectric polymer nanocomposites modified by DPA small molecular demonstrate over 150% enhancement in electrocaloric effect over the based terpolymer. And the present work leverages the interfacial coupling mechanism as a strategy to develop high-performance electrocaloric composites for solid-state refrigeration applications.

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