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Polymeric nanocomposites for electrocaloric refrigeration

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Abstract Electrocaloric refrigeration represents an alternative solid-state cooling technology that has the potential to reach the ultimate goal of achieving zero-global-warming potential, highly efficient refrigeration, and heat pumps. To date, both polymeric and inorganic oxides have demonstrated giant electrocaloric effect as well as respective cooling devices. Although both polymeric and inorganic oxides have been identified as promising cooling methods that are distinguishable from the traditional ones, they still pose many challenges to more practical applications. From an electrocaloric material point of view, electrocaloric nanocomposites may provide a solution to combine the beneficial effects of both organic and inorganic electrocaloric materials. This article reviews the recent advancements in polymer-based electrocaloric composites and the state-of-the-art cooling devices operating these nanocomposites. From a device point of view, it discusses the existing challenges and potential opportunities of electrocaloric nanocomposites.

Keywords nanocomposites, electrocaloric, refrigeration, polymer

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Special Column: Caloric Refrigeration for Zero-carbon Active Cooling and Heating

1 Introduction

Conventional refrigeration based on the vapor compression (VC) technology has been widely used in modern society. As there is a continuous rise of extreme weather recent years, the average number of air conditioner (AC) units per household is expected to rise as well as the overall electricity consumption in the department of AC and refrigeration. Considering the fact that most of the vapor-compression-based refrigerators are still generating strong greenhouse gases, the equivalent CO₂ emission due to the AC and refrigeration would reach up to 45% of the total CO₂ emission in 2050 [1,2]. To achieve the goal of carbon neutrality without reducing the life standard for the general public, many countries are eager to develop new alternatives for zero global warming potential, and highly efficient cooling and heating.

The electrocaloric (EC) cooling technology may be the solution to the problem. Empowered by the giant electrocaloric effect (ECE) that was predicted over one decade ago, EC refrigeration represented a new type of electric-driven, solid-state refrigeration that generates reversible dipolar entropy changes by alternating the polarization-depolarization process of dielectric materials, thereby realizing a thermodynamic cycle for cooling and heat pumping. As a capacitive field-effect in insulating materials, the energy reversibility of the EC cooling technology is intrinsically high (> 90%), and the theoretical COP can reach 80% of the Carnot COP [2, 3]. In addition, the EC working body is capable of directly utilizing electricity in a highly efficient manner, implying a potential advantage in integrating the technology into the existing infrastructure and household. Despite a handful theoretical work on electrocaloric fluids and 2-D materials, the most applicable materials reported are ferroelectric oxides and polymers. At this stage, both EC inorganics and organics have demonstrated a large ECE and have been applied in the EC devices that exhibit a meaningful cooling ability.

Compared to their inorganic counterparts, EC polymers are known for their inherited feature as light, pliable soft materials. In addition to the ECE, these multifunctional soft materials have been extensively studied for their giant electromechanical energy coupling in the fields of sensing and actuating. These unique functions would enable potential applications in which the traditional VC technology is too bulky and heavy to fit in, e.g., on-chip thermal management, wearable refrigeration and heat pump, micro-refrigeration devices, and customized, localized thermal management of electric vehicles.

There still exist many challenges to make the intriguing new cooling technology more applicable. The first electrocaloric effect refrigeration device was designed by Russian scientists in 1992, utilizing ferroelectric ceramics, even before the discovery of the giant ECE. In 2013, shortly after the first report of direct measurement of the giant electrocaloric effect using the thermocouples, Gu et al. first reported an electrocaloric refrigerator employing a multi-layered EC polymer (irradiated PVDF-TrFE, 68/32 mol%) as the working body [4]. The device exhibited a T_{span} of over 6.6 K that was still comparable with some of the most recent research work on EC devices.

If operating an EC refrigeration cycle, an electrocaloric device extracts heat from the heat source and puts it into the heat sink. Ideally, an efficient and fast heat transfer would allow the device to achieve a large cooling power (CP) and coefficient of performance (COP). From the point of view of the device, the thermal conductivity, mechanical and electrical stability, conduction and hysteresis loss, etc. are equally important to the giant ECE (including the entropy change ΔS and the temperature change ΔT). As the neat EC polymers are never outstanding for their thermal conductivity, and considering the inevitably persistent ferroelectric hysteresis in the relaxor ferroelectric polymers (especially at high fields), designing the EC nanocomposites with extrinsic nanofillers to provide the above-mentioned additional features has become a rational methodology in the field.

This paper reviewed the recent development status of electrocaloric nanocomposites and the EC devices that were utilizing the polymeric working bodies. It categorized different types of electrocaloric nanocomposites, and summarized their key properties that mattered for the EC cooling devices, i.e., electrocaloric performance, thermal conductivity, breakdown field, and other dielectric and mechanical performances. Figure 1 shows the most important properties of the EC cooling device. In addition to the recent advances, it also discussed the existing challenges and potential routes to further enhance the overall properties of the electrocaloric nanocomposites.

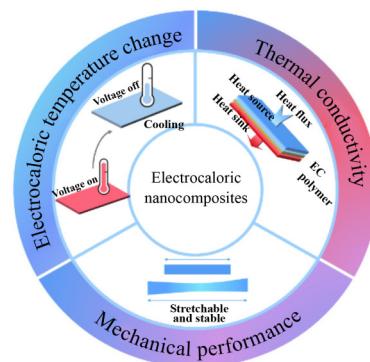


Fig. 1 Electrocaloric nanocomposites for a more applicable device with a good electrocaloric effect, thermal conductivity, and mechanical performance.

2 Development of electrocaloric polymers as base materials for nanocomposites

Electrocaloric effect materials are mainly divided into inorganic ceramic materials and organic polymer-based materials. In 2008, Neese et al. [5] at the Pennsylvania State University discovered giant ECE in polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE, copolymer, 55/45 mol%) films and poly (vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (PVDF-TrFE-CFE, terpolymer, 59.2/33.6/7.2 mol%) films.

The ECE performance of normal ferroelectric polymers reaches the maximum value at the phase transition temperature T_c (or called Curie temperature). When the temperature deviates from the phase transition temperature, the ECE performance will deteriorate. The electric field-induced polarization change is weaker at a lower temperature than that of T_c because of the larger remnant polarization caused by the micrometer-scale ferroelectric domains [6–8]. When the temperature is higher than T_c , the ratio of the paraelectric phase increases rapidly with the increase of temperature, which reduces the maximum polarization, resulting in a poor ECE performance. Normal ferroelectric polymers with ECE properties consist of PVDF-TrFE (copolymers) with various molar ratios. PVDF-TrFE 55/45 mol% is the most commonly used one, which has a second-order phase transition ferroelectric polymer, with no thermal hysteresis and a low Curie temperature (approximately 70 °C). Compared with commercial relaxor ferroelectric P(VDF-TrFE-CFE), the manufacturing control of the copolymer can be much easier and can achieve a higher electrocaloric effect performance around the Curie temperature. However, the copolymers exhibit a narrow operating temperature range (near its Curie temperature) and their Curie temperatures are normally much higher than the room temperature, which results in a poor electrocaloric effect performance for room temperature applications. Therefore, researchers have been trying to destabilize the ferroelectric phase of the polymers and

obtain a large ECE over the wide temperature window around room temperature [9–15]. The most effective method can be described as defect modification. By irradiating the copolymer or introducing a suitable third or fourth monomer into the polymeric chain, the engineered defects in the polymer matrix break the bulky ferroelectric domain, resulting in a series of relaxor ferroelectric polymers [6] that can provide a large and reversible polarization during the poling and de-poling cycles.

There is no strict first-order phase transition in relaxor ferroelectrics, and the phase transition occurs in a large temperature range, triggered by external electric fields. Therefore, it can maintain a large ECE performance within a large temperature range. There are randomly oriented polar nano regions (PNR) in relaxor ferroelectric materials with a small polarization hysteresis.

At present, the terpolymer P(VDF-TrFE-CFE) is the most widely and intensively studied electrocaloric polymer, due to the relatively large ECE and wide operation temperature range at room temperature. Some of these relaxor ferroelectric polymers have been commercialized for EC research and applications [16, 17]. Besides the above-mentioned advantages as a flexible material, one of the attractive features of the polymer is that it can be processed at low temperatures, using various types of commercially available fabrication methods (solution-based methods, hot press, etc.). Compared to the high processing temperature of most inorganic EC materials (over 1000 °C at which the polymer would not survive [18–24], the low-temperature fabrication methods make the polymer a widely applied host for extrinsic inorganic fillers to join, and each participant could hold their respective intrinsic properties inside the nanocomposites. The polymeric nanocomposites are therefore accessible to various design

methods and could enhance the overall properties for a better working body of solid-state refrigeration [25, 26].

3 Types of electrocaloric nanocomposites

Electrocaloric nanocomposites could be categorized into polymer-polymer composites and polymer-inorganic composites. Table 1 and Fig. 2 summarize the ECE performance of some polymers and electrocaloric nanocomposites.

3.1 Polymer-polymer blends

Polymer-polymer composites are usually made by mixing various types of polymers, with the goal to produce a better ECE, and stronger dielectric and mechanical performances. The participating polymers are required to be miscible to each other in order to generate polymeric films with high qualities. Currently, the P(VDF-TrFE-CFE)-based relaxor ferroelectric polymers are believed to be the state-of-the-art EC polymer that is already commercially available. Therefore, the PVDF-based copolymers were frequently selected as the rational choices for participating polymers. Without the defect modification provided by the CFE monomer, the P(VDF-TrFE)s (VDF > 55 mol%) are known for their spontaneous ferroelectric behaviors. As mentioned before, normal ferroelectric materials only exhibit the large EC induced entropy change near the phase transition temperature. At room temperature, the strong spontaneous polarization of the copolymers make them highly irreversible during poling and de-poling processes. However, as a participating polymer inside the polymer blends, they could provide an interfacial polarization effect due to the smaller permittivity compared to the terpolymers, as well

Table 1 Summary of key properties of EC nanocomposites

Material	T/K	$\Delta E/(MV \cdot m^{-1})$	$\Delta S/(J \cdot (kg \cdot K)^{-1})$	$\Delta T/K$	$k/(W \cdot (m \cdot K)^{-1})$	Ref.
Copolymer P(VDF-TrFE)55/45 mol%	353	200	60.8	12.6	–	Neese et al. [5]
Terpolymer P(VDF-TrFE-CFE)59.2/33.6/7.2 mol%	303	100	37.8	7.6	–	Li et al. [27]
P(VDF-TrFE-CFE)/PMN-PT	303	180	150	31	–	Li et al. [28]
P(VDF-TrFE-CFE)/BNNs/BST67	303	250	210	50.5	–	Zhang et al. [29]
P(VDF-TrFE-CFE)/BNNs/BST1/2/3	273–333	200	170	35	–	Zhang et al. [30]
P(VDF-TrFE-CFE)/BST(NWs)	Room temperature	100	96	19.5	–	Zhang et al. [31]
P(VDF-TrFE-CFE)/AAO	Room temperature	50	12	2.5	6	Zhang et al. [32]
P(VDF-TrFE)/BST	351	60	/	2.5	–	Jiang et al. [33]
P(VDF-TrFE-CFE)/graphene	Room temperature	40	24.8	5.2	–	Yang et al. [34]
P(VDF-TrFE-CFE)/BST_nfs	303	200	105	44.3	–	Qian et al. [35]
P(VDF-TrFE-CFE)/BTSn11	Room temperature	100	44	9.08	–	Lu et al. [36]
P(VDF-TrFE-CFE)/BFBZT	303	75	78	13.8	–	Chen et al. [37]
Polymer/BST NW array	Room temperature	60	16.3	10.1	/	Zhang et al. [38]

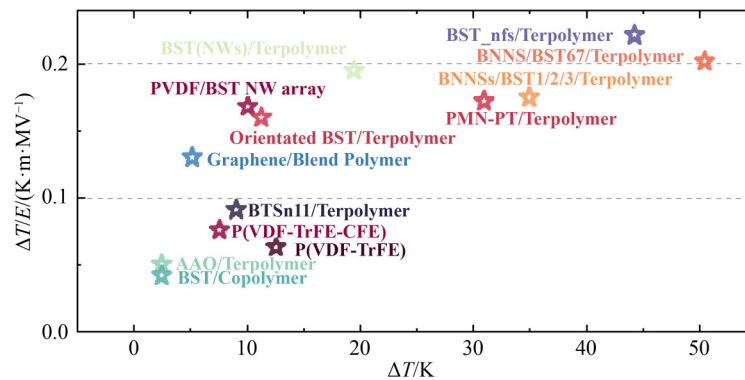


Fig. 2 Summarized EC temperature changes and EC strengths achieved in different materials and the corresponding electric field.

as the internal built-in electric fields due to their remnant polarization after the proper poling processes [39–43]. Moreover, the copolymer and the terpolymer are well miscible with each other. Considering the fact that the normal ferroelectric copolymer are also exhibiting higher modulus compared to the terpolymer [12,44], the synergy between the base terpolymer and the additional copolymer would be helpful for the practical application of electrocaloric effect refrigerators.

In 2012, Chen et al. [12] mixed relaxor ferroelectric material PVDF-TrFE-CFE 62.5/29/8.5 mol% with 10 wt.% normal ferroelectric material PVDF-TrFE 55/45 mol%. This blend increased the crystallinity by 10% and the adiabatic temperature changed to 30% over the entire experimental temperature (20–60 °C). A series of polymer-polymer composites were reported by blending PVDF-TrFE-CFE 59/33/8 mol% with PVDF-TrFE 65/35 mol% (90/10 mol%) [14,39]. This trial shows that the composites can generate a much larger electrocaloric effect in lower applied electric fields, due to the internal electric field introduced by the ferroelectric copolymer (10 mol%).

As expected, keeping increasing the content of the copolymer would result in the competition between the relaxor and the normal ferroelectricity, and the increase of the ferroelectric hysteresis. Interestingly, distinguished from the ferroelectric hysteresis in the normal ferroelectric material, which could only be stable in two states (polarization up and polarization down), the existence of the relaxor terpolymer would help the polymer blend stay at a state of polarization zero, during the de-poling process. Based on this, Qian et al. [15] designed a hybrid normal ferroelectric/relaxor ferroelectric polymer blend (50/50 mol%) in which the polymer blend in the poled state could be de-poled to the polarization-zero state, and exhibited an anomalous negative electrocaloric effect that provided only a cooling effect after triggered by one complete pulse of the electric field. The anomalous negative electrocaloric effect could be applied as a storage material for cooling as a cooling battery that can provide imminent cooling on demand.

In addition to the blending system with ferroelectric

polymers, the P(VDF-TrFE) based copolymers and terpolymers were frequently blended with other dielectric polymers such as PMMA, P(VDF-HFP), etc., to enhance the piezoelectric properties and energy storage for niche applications [46,47]. It is expected that extended research effort would be made on the various polymer-polymer nanocomposite systems for acquiring a large ECE and balancing the overall properties.

It is worth highlighting that enhancement of the ECE in the polymer blends directly benefited from the capability of low-temperature processes in the participating polymers. The normal ferroelectrics and the relaxor ferroelectrics could maintain and synergically provide their unique properties in blend films [14], with no intermediate product generated during the mixing process [48,49].

3.2 Polymer-inorganic composites

Compared to the limited selection of ferroelectric polymers, inorganic materials provided a huge pool of filler candidates [28–31,33–38,45,50,51]. Most of the choices were focused on the inorganic ferroelectric oxides, owing to their high dielectric constant and their nature as electrical insulators. During the cycling of the EC working bodies, conduction loss is one of the most significant factors that would deteriorate the performance of the device. Therefore, in the current research on electrocaloric nanocomposites, various ceramic nanoparticles are commonly used. Since ferroelectric ceramics possess a high thermal conductivity [29,30,52] and a large entropy change at low electric field [53–55], ferroelectric ceramics are the most important fillers in the research of polymeric EC nanocomposites.

Lu et al. [36] prepared PVDF-based composite electrocaloric films, in which BTSn11 was used as the filler, and the ECE performance in the composites was enhanced by about 50% and 1400% compared with pure terpolymer and BTSn11 ceramics. Qian et al. [35] prepared P(VDF-TrFE-CFE)/BZT composite films with a better ECE performance than pure terpolymer films, which was attributed to the interfacial coupling of dipoles at the filler/polymer

interface. Figure 3(a) shows the SEM images of the surface of the film for nanocomposites. Although most of these researches attributed the enhancement of the ECE to the interfacial effects, whether these participating ferroelectric nanoparticles contribute to the ECE by their intrinsic ECE, is still not clearly explained.

Kang et al. [56] prepared BST nanoparticles/BNNSs/ferroelectric polymer composites for electrocaloric cooling using the grafting technology as demonstrated in Fig. 3(b). The composites not only increased the polarization but also increased the breakdown strength and thermal conductivity.

In addition to compounding through inorganic nanofillers, there are other methods using structure to realize compounding. Zhang et al. [38] prepared BST nanowire array on soft substrates (e.g., PDMS), as displayed in Fig. 3(c). This novel nanostructured array generates a great ECE in low electric fields with outstanding pliability for potential application in wearable cooling devices. Zhang et al. [32] employed a new composite method to pour P(VDF-TrFE-CFE) (62.3/29.9/7.8 mol%) into anodic aluminum oxide (AAO) nanotube arrays, as manifested in Fig. 3(d). Due to the presence of AAO, the polymer-based inorganic composite electrocaloric films exhibit a higher thermal conductivity and a better ECE performance for the EC-active polymers filling into the AAO template (EC-inactive AAO were excluded during the calculation of ΔT), than the random oriented pure terpolymer films. In 2020, Pei et al. [57] designed self-actuating electrocaloric cooling fibers, which placed P(VDF-

TrFE-CFE) between conductive fiber core electrodes and single-walled carbon nanotubes. This fiber design allows EC coolers to move heat from one location to another without pumps, providing important opportunities for future implementation of the EC cooling device.

Despite electrical insulating fillers, there are a few research attempts by designing the EC nanocomposites with conductive fillers, such as by incorporating the nano-scaled metallic particles and carbon-based nanomaterials to construct percolation systems [34,58–61]. In the mixture of P(VDF-TrFE-CFE) and P(VDF-TrFE) (90/10 wt%), Yang et al. [34] achieved a large electrocaloric effect in low field by incorporating graphene nanofillers. To block the electrical conduction path, polymeric nanocomposite films were uniaxially stretched. The fabrication process was proven to be successful in reducing the conduction loss of the graphene-incorporated EC nanocomposite.

It is observed that, currently, most of the EC nanocomposites reported in the literature are simple mixtures. Some of the inorganic nano-fillers were treated to include functional groups that could lightly interact with the PVDF-based polymers via hydrogen bonds [62, 63]. Therefore, organic-inorganic interfaces were weaker and had limited control of the defects at the interface. Covalently bonding of the nanofillers to the polymer matrix may help provide a stronger and more controllable interface, in order to enhance the mechanical and dielectric stability of the EC nanocomposites, which should be equally important for practical applications.

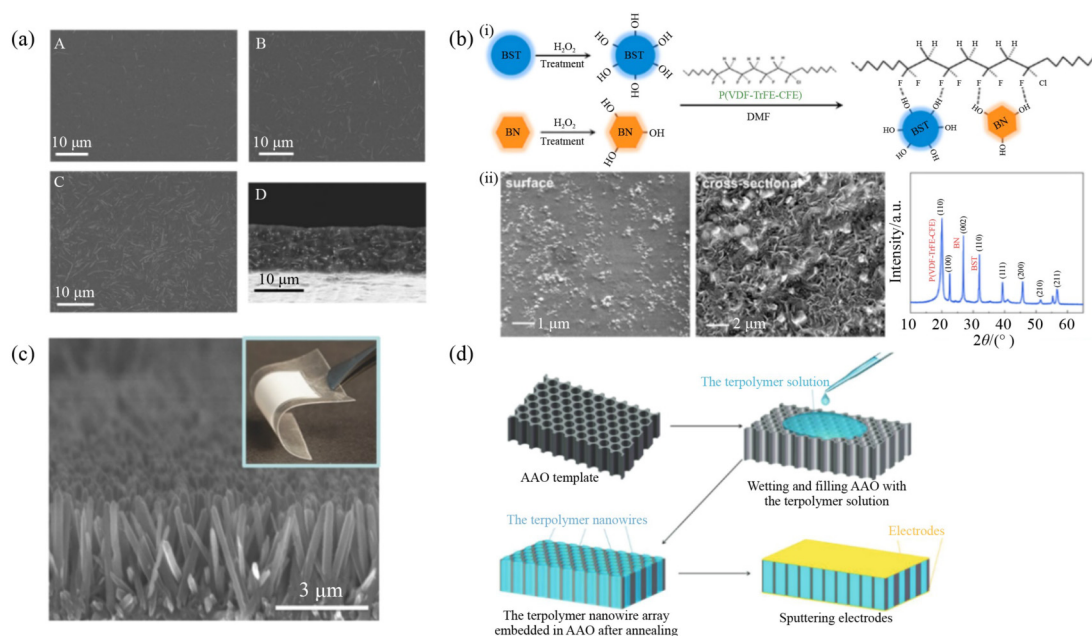


Fig. 3 Recent advances in electrocaloric nanocomposites.

(a) SEM images of surface of film the nanocomposites; (b) schematic diagram of synthesis of nanocomposite using grafting method; (c) cross-sectional view of BST NW array on PVDF; (d) schematic illustration of preparation of the polymer nanowire array. (Reprinted with permission from Refs. [32,35,38,56], Copyright 2019, 2018, 2016 Wiley; 2021 Elsevier, respectively.)

4 Electrocaloric effect in electrocaloric nanocomposites

EC-induced temperature change is the direct result of the electrocaloric effect, which is, therefore, the enabling property of the cooling system. Although EC materials should ideally be a perfect electrical insulator, realistic EC materials always contain multiple sources of energy loss, which inevitably become the additional heat that demise the EC-induced temperature change. The idea of making nanocomposite would normally enhance the conduction loss owing to the defects they unintentionally introduced if not properly designed. In addition, the agglomeration of nanoparticles may further introduce electronic conduction which can lead to significant dielectric loss. Carefully choosing and designing the nanofillers would ease the enhancement of the dielectric loss in the nanocomposites. Li et al. [64] found that PVDF-TrFE-CTFE with and without the addition of TiO₂ had a similar dielectric loss. In addition, electrical insulated 2D materials, e.g., boron nitride nanosheets, were proven to be able to block the electron injection and hopping through the nanocomposite, inducing a much higher dielectric strength compared to that of the base polymer [65].

After introducing inorganic nanofillers in polymers, in general, interfacial polarization is introduced due to the discrepancy in permittivity between fillers and the polymer matrix. When the electric field is applied, the charges accumulate at the interface of the two participating materials, which have different features of permittivity and dielectric loss, thus resulting in a field-induced interfacial polarization. As the number of charges accumulated at the interface increases, the space charge density increases, which further enhances polarizability.

The effects of nanofillers in the nanocomposites on the micro- to nano-scale of dielectric properties mainly include the concentration, size, and topology effect. For percolating composites composed of conductive fillers in the insulating polymer matrix, near the threshold region, small percolation concentrations can significantly change the dielectric properties of the composites, i.e., the dielectric constant K will be significantly higher than that of the matrix K_m , whose formula is

$$K = K_m f_c / (f_c - f)^q, \quad (1)$$

where f is the filler content, f_c the percolation threshold for the conductive filler, and q the critical exponent (about 1 for 3D composites), respectively [66,67]. Earlier studies indicated that in addition to the percolation effect enhancing the dielectric response, the large dielectric contrast between the conductive nanofillers and the polymer matrix also produced interfacial effects [34,58,68,69]. Therefore, to maximize the interfacial effect, nanofillers with a large specific surface area are

required. Chen et al. [37] found that induced by the mismatch of dielectric constants between BFO and BZT, electrical polarization of the BFO@BZT_nfs gained much enhancement due to the concentration of the local electrical field. Figure 4(a) depicts the dielectric and electrocaloric properties between nanocomposites filled with different nanofillers.

The size of the nanofillers is an important feature. The understanding the effect of filler size and size distribution leads to an in-depth study of the dielectric properties of the composites. Smaller-sized fillers result in significantly enhanced interfacial areas inside composites. To obtain new properties of polymer composites, processing methods that control particle size distribution, dispersion, and interfacial interactions are critical. Morozovska et al. [70] chose BaTiO₃ nanoparticles as fillers placed into a polymer matrix to perform numerical simulations. They found that the maxima of electrocaloric temperature variation can be induced by changing the nanoparticle size and it is possible to select the range of particle radii to gain the maximal EC energy conversion at room temperature.

Fillers of different shapes or topologies have different surface areas, resulting in different interfacial areas in the composites, and thus different interfacial polarizations and different dielectric properties. Zhang et al. conducted research on different shapes of BST fillers, including nanocubes, nanorods, nanowires [30]. Figure 4(b) shows the Q , ΔT , and ΔS of P(VDF-TrFE-CFE)-based composites with different shapes of fillers at 100 MV/m. Not only was it found that, by exploiting the synergistic effect of ceramic nanofillers and polymer matrix, polymer nanocomposites could work efficiently at moderate and high electric fields to achieve remarkable electrocaloric performance, but also, from this study, it was found that the electrocaloric performance was closely dependent on the morphology of the nanofillers, which provided additional avenues to enhance the electrocaloric effect performance.

To investigate the electrical properties localized at the interface, currently, there are several advanced characterization and simulation tools available. *In situ* piezoresponse force microscope (PFM) was employed to explore the topographic image of composites and phase-field simulation to study the mechanism of interfacial coupling [35]. Figure 4(c) shows the phase-field simulation of polarizability for the nanocomposite with 10 vol% of BZT_nfs. The great difference between considering and not considering the interfacial polarization reveals the fact that the interfacial coupling plays a key role in rendering a larger dielectric response and electrocaloric performance. Figure 4(d) suggests that the fast relaxation process of the dipole could be well distinguished by the *in-situ* PFM.

Although there exist multiple models to describe the behaviors of the interface in the dielectric nanocomposite,

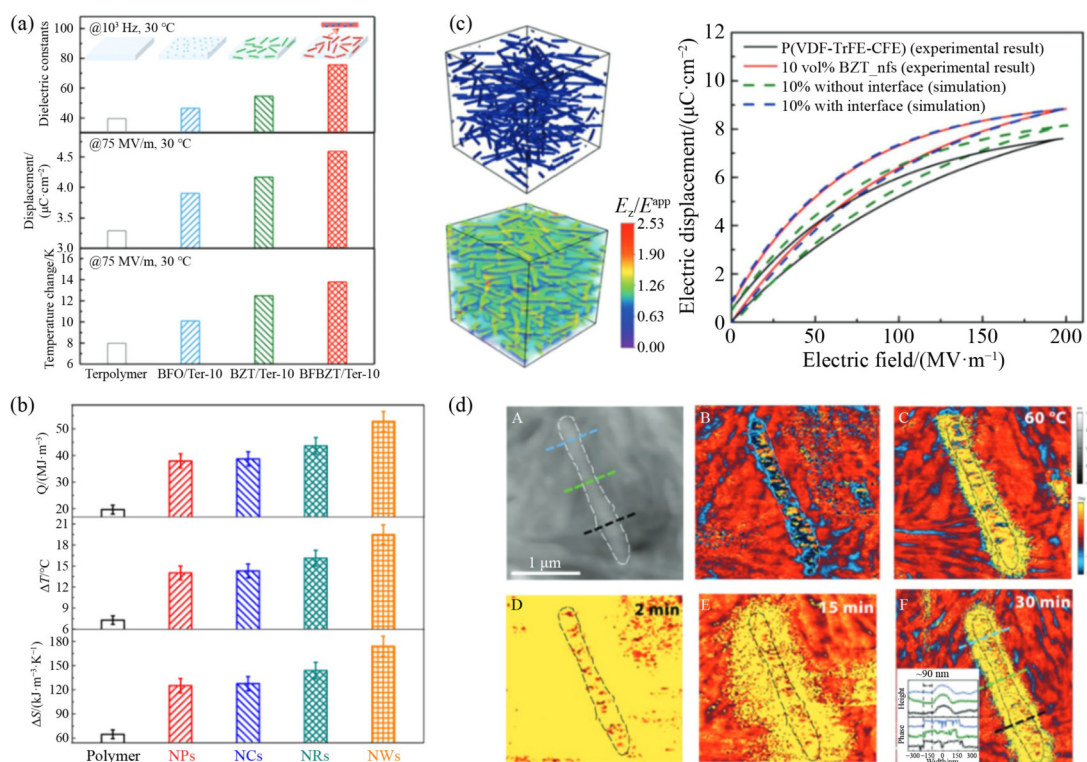


Fig. 4 Interfacial research.

(a) Comparison of dielectric and electrocaloric properties between nanocomposites filled with different nanofillers; (b) comparison of electrocaloric properties between nanocomposites filled with different shape nanofillers; (c) phase-field simulation of polarizability for nanocomposites; (d) *in situ* PFM image of nanocomposites. (Reprinted with permission from Refs. [31,35,37], Copyright 2015 ACS; 2018, 2020 Wiley, respectively.)

including the dielectric double-layer structure, the multi-core model, and the single-layer model, etc., their correlation to the electrothermal cross-couplings (pyroelectric and electrocaloric effect) have not yet been fully disclosed.

The mechanism of the dielectric double-layer structure in the nanodielectric was widely accepted, proposed in Ref. [71]. In polymer composites, polymer chains and nanoparticles are connected through chemical bonds or physical interactions, and an interface is formed between the two phases. When an external electric field is applied, the nanoparticles accumulate charges on their surfaces due to charging, and the surrounding phase responds by creating a shielding layer that accumulates charges opposite to those on the nanoparticles, thereby inhibiting the accumulation of charges on the nanoparticles. Due to the Coulomb force, the charged nanofillers will be free charges in the polymer matrix, rearranged into a dielectric double layer (stern layer and diffuse layer) around it, as presented in Fig. 5(a). The stern layer is formed by the electric charges on the surface of the nanoceramic particles attracting the opposite charges in the polymer matrix, and the diffuse layer is formed by the remaining carriers in the polymer matrix at the periphery of the adsorption layer. The properties of the diffuse layer

are immaterial to the dielectric properties of the polymer-based nanocomposites. On the one hand, under the action of the electric field, the carriers in the diffuse layer will migrate to form a space charge polarization; on the other hand, when the nanoparticle content reaches the percolation threshold, the charge carriers will migrate along the diffuse layers of different particles to form a conductive path, resulting in a relatively large leakage current.

The multi-core model was proposed by Tanaka et al. from Waseda University based on chemical, electrical and morphological theories [72,73]. As shown in Fig. 5(b), it is under the assumption that the filler in the composite material is spherical, and the interface between the filler and the matrix forms a three-layer structure of bonded layer, bound layer, and loose layer from the inside to the outside, respectively.

The single-layer model was proposed by Lewis based on the dielectric double-layer theory of colloidal chemistry [74], as shown in Fig. 5(c), where A is the filler, B is the matrix, and AB is the interface between the filler and the matrix. Assuming that filler A is uniformly dispersed in the matrix, the surface of filler A is charged due to the ionization of surface groups or the adsorption of particles in the matrix. At this time, substrate B

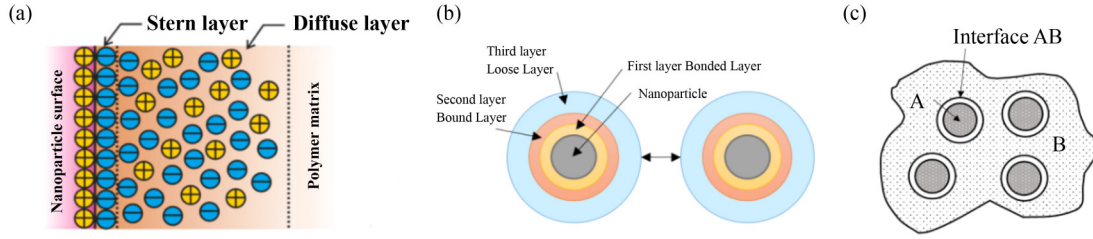


Fig. 5 Interface model.

(a) Dielectric double-layer structure; (b) multi-core model; (c) single-layer model. (Reprinted with permission from Ref. [71], Copyright 2016 ACS.)

generates charges accordingly. If phase A is a particle of finite size and surrounded by B, there is an AB interface between them. As the particle diameter decreases, the interface properties become more and more prominent.

The above models provide tools to understand the dielectric properties of polymer composites to a certain extent, as many dielectric phenomena are well explained. However, the interfacial effects were introduced to the electrocaloric effect. Some enhancements of the ECE were simply explained by the increasing polarization induced at the interface. As there are quite different types of polarization, the introduction of the most efficient ones to contribute to the electric field-induced polar entropy change still poses a challenge. The detailed study of the interface would elaborate on the origin of the ECE in dielectric nanocomposites in the future.

5 Thermal and mechanical performances

When designing an EC working body with nanocomposites for the EC cooling device, it is important to extract the heating and cooling effect as fast as possible from the material to the external media, in order to achieve a higher cycling frequency and hence a large cooling power. In addition, a strong mechanical property would facilitate a good thermal contact through a solid-solid interface for heat transfer. Therefore, the thermal conductivity and mechanical performance are equally important compared to the EC temperature change in making an applicable electrocaloric effect cooling device [75,76].

Considering the fact that most of the EC working bodies are designed in the forms of plates and films, the heat transfer is along the thickness direction of the working bodies. For a given cycling frequency, the largest thickness for a complete heat transfer can be referred to as the thermal diffusion (penetration) length δ , which is given by

$$\delta = \sqrt{\frac{k}{\pi f \rho c_L}}, \quad (2)$$

where k refers to the thermal conductivity, f the

frequency, ρ the density, and c_L the lattice heat capacity. However, the thermal conductivities of PVDF-based terpolymer are about 0.2 W/(m·K) [77]. The low thermal conductivity of polymers requires a longer time for achieving a high-efficiency heat transfer, if the thickness of the film is a constant, therefore limiting the actual performance of the application despite the giant electrocaloric effect, especially considering the large thickness (typically over 500 μm) of a working body rather than a single sheet of thick polymeric film (typically below 50 μm).

Since the electrocaloric cooling device realizes heat-pumping utilizing an electric field to induce a dipolar order-disorder phase transition, a more disordered structure implies a larger dipolar entropy state at the zero-field, which could lead to a large ECE. However, a high thermal conductivity may need an ordered arrangement of atomic/molecular structures. In crystalline polymers, thermal transport would be efficient along chain directions, which means if the polymer is more ordered, it would have a higher conductivity. Contradictions arise when it is purposed to increase the thermal conductivity and enhance the electrocaloric effect at the same time.

In addition, according to the kinetic theory and the Newton-Laplace equation, the thermal conductivity of a material would be influenced by the elastic modulus of the material [78,79]. The relationship between the elastic modulus and the thermal conductivity of the material is shown in Eq. (3),

$$k = \left(\frac{E}{\rho}\right)^{\frac{1}{2}} \left(\frac{c_v l}{3}\right), \quad (3)$$

where E refers to the elastic modulus, ρ the density, c_v the volumetric heat capacity and l the average mean free path of phonons. The thermal conductivity of the polymer could be enhanced by the macromolecular chain alignment, which would lead to a surge of elastic modulus and then a decrease in the flexibility of the polymer. Therefore, the preparation of polymers possessing a high thermal conductivity without losing their flexibility remain a tough challenge.

One attempt at this fundamental contradiction in soft materials is making composites with various fillers. By

incorporating proper fillers in an optimized topology and orientation, not only thermal conductivity but also dielectric properties and electrocaloric effect performance can be enhanced. In 2015, Zhang et al. [29] prepared a P(VDF-TrFE-CFE)-based nanocomposite using two-dimensional boron nitride nanosheets (BNNS) and BSTO as fillers to enhance the thermal conductivity and breakdown the electric field. The improvement of the thermal conductivity and breakdown of the electric field arising from the fillers may lead to a higher cooling power density in the electrocaloric nanocomposites refrigerator. Three years later, Zhang et al. [30] prepared a P(VDF-TrFE-CFE)-based nanocomposite also using two-dimensional boron nitride nanosheets (BNNS) with BST nanowires instead of sphere BST67 particles. This change of morphology of the nanofillers increases the thermal conductivity from 1 W/(m·K) to 1.2 W/(m·K) and both have a great electrocaloric effect performance. The structural change would also assist to improve the thermal conductivity. Zhang et al. [32] made films by pouring P(VDF-TrFE-CFE) (62.3/29.9/7.8 mol%) into an anodic aluminum oxide (AAO) nanotube. High-temperature annealed AAO membrane with a high thermal conductivity is heat-transfer channels. The thermal conductivity of this composite has a great increase to 6 W/(m·K). Li et al. [80] designed an interpenetrating architecture of EC polymer, making a 300% increase in the thermal conductivity over neat polymers.

Besides of the handful research focusing on the thermal conductivity in the EC nanocomposite, less research was conducted that paid attention to the mechanical performance. Zhang et al. [31] not only focused on the topology of the nanofillers but also tested Young's modulus and obtained the mechanical collapse breakdown electric field $E_{b(\text{mech})}$ by adopting Eq. (4).

$$E_{b(\text{mech})} = 0.606 \left[\frac{Y}{\varepsilon_0 \varepsilon_r} \right]^{1/2}, \quad (4)$$

where Y is Young's modulus, ε_0 is the vacuum permittivity and ε_r is the relative permittivity of the nanocomposites. The result of the present paper indicates that the higher modulus of composites leads to a larger electromechanical $E_{b(\text{mech})}$. However, it does not mention the thermal conductivity.

6 Summary and pespective

The electrocaloric refrigeration was recognized as a strong candidate for the next generation of refrigeration, in which the electrocaloric nanocomposites material had the potential to concurrently achieve a large ECE, a high thermal conductivity, flexible and strong mechanical properties that neither the inorganic nor the polymeric material could solely achieve. In addition, the polymer-

based EC nanocomposite could be easily fabricated into many forms to integrate into the working bodies of refrigeration. To further improve the EC performance for the solid-state refrigerant, it is important to review where the research field is at in terms of EC devices.

There have been some trials for the electrocaloric cooling device that is operating EC soft materials as solid-state refrigerants. Gu et al. [4] successfully fabricated a polymer-based ECE refrigerator in 2013, which realized a temperature span of more than 6 K across a 2 cm long device, as shown in Fig. 6(a). It is the first demonstration of a polymeric refrigerator operating a pair of working bodies that is essentially multilayered polymer capacitors, whose temperature span is still competitive compared to the recently reported, all-solid EC device utilizing the multilayered $\text{PbSc}_x\text{Ta}_{1-x}\text{O}_3$ (PST) ceramics [81,82]. Guo et al. [83] employed the finite element method (FEM) to explore the performance of the electrocaloric heat pumping system, utilizing P(VDF-TrFE-CFE) as the imaginary working body, as shown in Fig. 6(b). Their analysis suggested that time lag would significantly affect the cooling power. These EC devices were operating an active electrocaloric regeneration (AER) cycle by which the device could reach a wider temperature span than the temperature life of the working body. During the refrigeration cycle, the EC material works as a stationary core to provide the heat pumping ability, and another media (solid or fluid heat exchange material for regeneration) has to be introduced to carry the heat in a proper direction.

Some other designs of EC refrigerators relied on the movement of the EC working body itself to pump heat. In 2017, Ma et al. [1] developed an ECE refrigerator using the electrostatic actuation mechanism to provide the motion power to electrocaloric effect film. This device was reported to have a 2.8 K temperature span with a COP of 13, using the neat terpolymer P(VDF-TrFE-CFE) as the active EC material, as presented in Fig. 6(c). In addition, the design can be extended to a tandem structure that offers similar cooling power but a much wide temperature span owing to the cascading mechanism [84, 85]. Different from the prior discussed AER device, the heat was pumped along the direction of the film thickness rather than the in-plane directions. Due to the elegant control of the electrostatic actuation, which eliminated the requirement for the external motors or pumps to cycle the EC materials, these devices were more likely to be applied as miniature and even wearable cooling solutions.

During the development of the EC devices, a clear path of advancement was observed for the EC working bodies, i.e., from the homogeneous materials toward the nanocomposites. Bo et al. [85] incorporated the dioctyl phthalate (DOP) into the P(VDF-TrFE-CFE) to enhance the degree of freedom of the chain movement and hence improved the ECE for the device operation. The same group reported an EC device utilizing the heat exchange

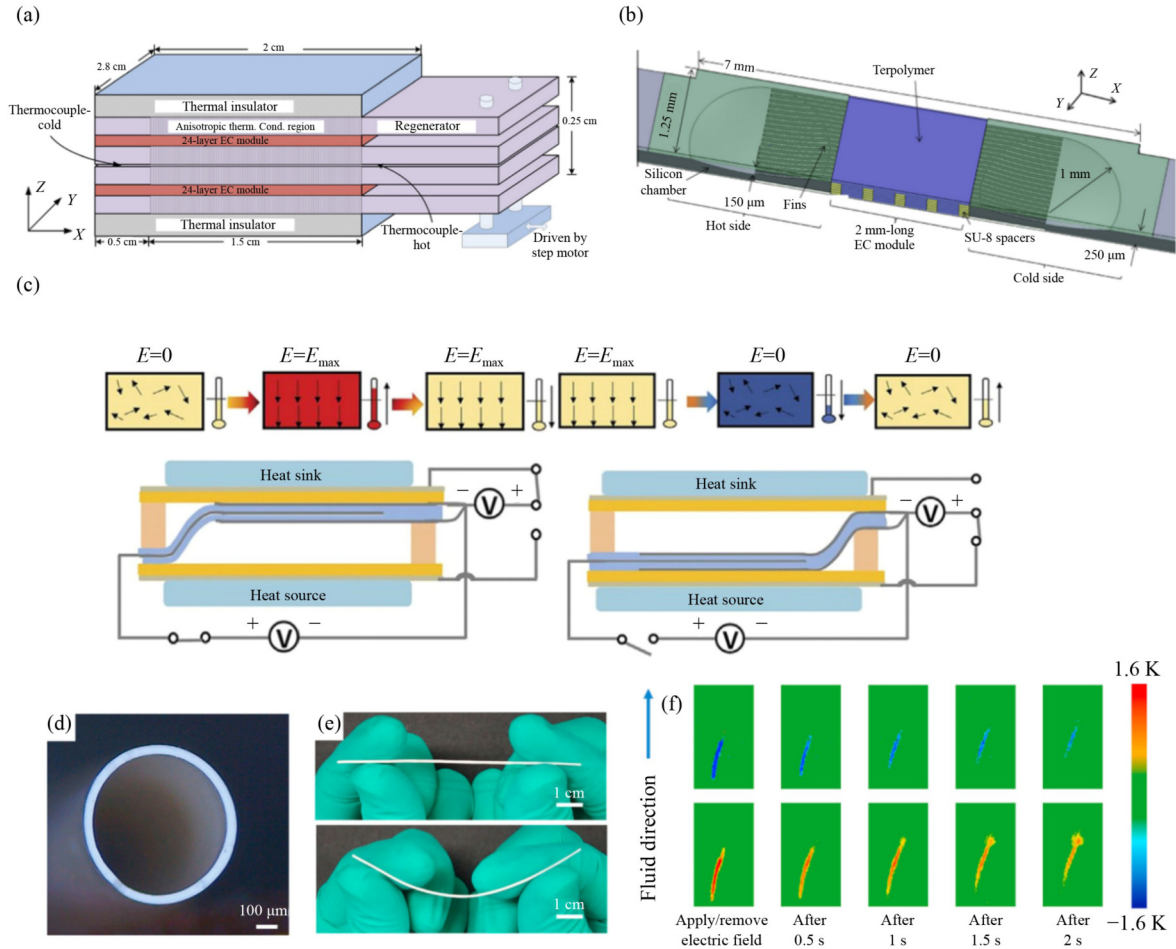


Fig. 6 EC cooling device based on polymers and their nanocomposites.

(a) Electrocaloric oscillatory refrigeration prototype; (b) simulation of fluid-solid coupling heat transfer; (c) electrocaloric refrigeration with an electrostatic actuation mechanism; (d–f) EC cooling capillary tubes. (Reprinted with permission from Refs. [1,4,83,86], Copyright 2017 AAAS; 2013 AIP; 2014 Elsevier; 2021 Elsevier, respectively.)

fluid to carry the heating and cooling to different locations. The heat exchange fluid was flowing in an EC-active tube that was fabricated via $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) nanoparticles filled (P(VDF-TrFE-CFE), by coaxial wet-spinning technology. The BST nanoparticles not only improve the EC performance of the tube but also increase the mechanical property of the polymer to form the capillary tube [86], as shown in Figs. 6(d)–6(f). As a result, the device achieved a device-specific cooling power of 702.1 mW/cm^3 .

Despite encouraging results discovered corresponding to the electrocaloric nanocomposites, the development of a highly efficient electrocaloric cooling device is still in its early stage. Much work remains to be done before more applicable applications can be deployed. Thus, the remaining challenges and where the opportunities lie for future research in this promising research field were summarized:

1) Thermal conductivity is always difficult for the polymer to have a highly efficient heat transfer. With the operation of the cooling device, more attention would be

paid to the thermal conductivity of EC materials. Electrocaloric nanocomposites would have a great potential to address the intrinsic issues of polymers.

2) As the interfacial effect can lead to an improved electrocaloric effect, in-depth characterization and simulation focusing on the localized interface of the electrocaloric nanocomposites are utterly important to understand the underlying mechanisms of such an improvement from the nano-micro-scale. Considering the large differences in the polarization between the polymer matrix and inorganic nanofillers, most of the high electric field would still be applied to the polymer rather than inorganic fillers. Would the intrinsic ECE of the fillers participate in the enhancement of the ECE in the nanocomposites? Is the enhancement more weighted on the topology [30,87] or the orientation of the filler and hence the interface [35]? These questions are frequently omitted in the literature and could be addressed by advanced characterizations and simulation tools such as *in situ* cryoTEMs, tapping AFM-IRs, phase-field simulation, etc.

3) Recently, it is reported that a series of nanocomposites achieved much enhanced dielectric constant and energy storage by incorporating ultra-low content of nanofillers into the polymer matrix, namely diluted nanocomposites [88–90]. Due to the enhanced dielectric properties, it is interesting to seek similar enhancement in the ECE by employing similar mechanisms. In addition, the low content of fillers would prevent the forming of undesired defects due to the inevitable conglomeration of fillers when their content was too high.

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