

# Microcellular Foaming-derived Superlight Ultra-high Molecular Weight Poly(vinylidene fluoride) Foams for Outstanding Thermal Insulation Applications

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**Abstract** Poly(vinylidene fluoride) (PVDF) foam has received widespread attention due to its high strength, and excellent combination of flame-retardancy, antibacterial performance, and chemical stability. However, the foaming ability of conventional PVDF is severely limited by its rapid crystallization kinetics and poor melt strength. Although ultra-high molecular weight PVDF (H-PVDF) theoretically offers prolonged melt elasticity favorable for foaming, the extremely high melt viscosity poses substantial processing challenges, and its foaming behavior has remained largely unexplored. To address these issues, this study proposes a novel fabrication strategy combining solvent casting with microcellular foaming to prepare H-PVDF foams. Dynamic mechanical analysis and differential scanning calorimetry reveal that extensive chain entanglements in H-PVDF impose constraints on crystallization and significantly enhance melt strength. By tuning the processing parameters, the distinctive foaming behavior of H-PVDF under various conditions is systematically elucidated. Remarkably, a record-high expansion ratio of 55.6-fold is achieved, accompanied by a highly uniform and fine cellular structure. The resulting H-PVDF foams exhibit a low thermal conductivity of  $31.8 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , while retaining excellent compressive strength, flame-retardancy, and hydrophobicity. These outstanding properties highlight the great potential of H-PVDF foams as the thermal insulation materials for applications in aerospace, energy infrastructure, and other extreme environments.

**Keywords** Microcellular foaming; Ultra-high molecular weight PVDF; Superlight; Thermal insulation; Flame-retardancy

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## INTRODUCTION

Microcellular polymer foams have become essential materials in modern society.<sup>[1–3]</sup> Through the synergistic effects of their microcellular structure and the inherent properties of the polymer matrix, these advanced porous materials exhibit exceptional characteristics such as high specific strength, elasticity, insulation, and selective permeability.<sup>[4–6]</sup> These properties have enabled their widespread applications in various fields, including transportation, packaging, sports equipment, sound and thermal insulation, and filtration systems.<sup>[7–10]</sup> Specifically, building energy consumption accounts for nearly 40% of global energy usage.<sup>[11]</sup> Moreover, lightweight thermal insulation materials are crucial for improving energy efficiency in the aerospace sector, where weight reduction is directly correlates with fuel savings and emission reductions.<sup>[12]</sup> Microcellular polymer foams effectively address these challenges by providing superior thermal

insulation and ultra-low density, thus playing a significant role in global energy conservation and environmental sustainability. In contrast, traditional thermal insulation polymer foams, such as polystyrene (PS) and polyurethane (PU), could not meet the demands for safety and efficiency in the construction and aerospace industries.<sup>[13,14]</sup> Consequently, the development of insulating polymer foams with enhanced safety has garnered increasing attention. These materials must possess not only enhanced lightweight property but also improved safety features, such as flame-retardancy and hydrophobicity, to ensure reliability and adaptability in extreme environments.

Poly(vinylidene fluoride) (PVDF) stands out among polymers due to its exceptional heat resistance, flame-retardancy, chemical stability, and biocompatibility.<sup>[15,16]</sup> Microcellular PVDF foams further enhance these intrinsic advantages through the porous structure, demonstrating considerable potential for safe and durable thermal insulation materials.<sup>[17–19]</sup> Various strategies have been proposed for fabricating PVDF foam to realize this application. However, traditional techniques, such as template etching or phase inversion, often introduce challenges such as template residues or toxic solvents.<sup>[20–22]</sup> In this regard, supercritical carbon

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dioxide (scCO<sub>2</sub>) foaming technology is widely considered as a superior method for producing PVDF foams, owing to its effective, environmentally friendly, and structure controllable nature.<sup>[23,24]</sup>

Due to the high flexibility of molecular chains, PVDF exhibit rapid crystallization kinetic and high crystallinity.<sup>[25]</sup> These characteristics impose strict requirements on foaming condition and limit the achievable expansion ratios. To address these challenges, researchers have explored various strategies, such as modification, blending, and the incorporation of nanofillers.<sup>[26–28]</sup> For instance, Hu *et al.* significantly improved the melt strength of PLA by random copolymerizing of LA and CEMs, and modifying the polymer topology, thereby enhancing the foaming characteristics of the PLA samples.<sup>[26]</sup> Chai *et al.* fabricated PLA/PTFE blends that promoted crystallization and viscoelasticity, further improving foaming ability due to the formation of reticulated *in situ* PTFE nanofibrils.<sup>[27]</sup> Xu *et al.* introduced multi-walled carbon nanotube into PVDF, promoting heterogeneous nucleation and enhancing foam structure by producing denser, more unique cells.<sup>[28]</sup> However, these strategies often involve complex processing steps, increase production costs, extend processing cycles, or diminish the intrinsic advantages of PVDF.

Recent studies have indicated that polymers with higher molecular weight exhibit superior foaming ability due to enhanced viscoelasticity during foaming, resulting from increased molecular entanglements and stronger inter-chain interactions.<sup>[29,30]</sup> Based on these findings, ultra-high molecular weight (H-PVDF) is expected to serve as a promising alternative to conventional PVDF for producing high-expansion ratio foams, retaining the inherent advantages of PVDF without the need for external additives, thus offering an effective solution. However, its extremely high melt viscosity imposes significant challenges in melt processing, and its foaming behavior has remained largely unexplored to date.

In this study, a novel strategy combining solvent casting and microcellular foaming is proposed to overcome the processing limitations of H-PVDF and fabricate ultralight foams with outstanding comprehensive properties. Initially, solid H-PVDF with specific shape were prepared *via* a solvent casting process. Microcellular H-PVDF foams with exceptionally high expansion ratio were developed using clean and energy-efficient supercritical carbon dioxide (scCO<sub>2</sub>) foaming technology, exhibiting excellent comprehensive performance. Then, the thermal behavior of the solid H-PVDF was analyzed using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Next, the scCO<sub>2</sub> foaming process was applied to achieve ultra-high expansion ratios and structural control in the H-PVDF foams. Subsequently, the crystallization behavior of the H-PVDF foams, prepared under various foaming conditions was further investigated using X-ray diffraction (XRD) and DSC. Finally, the foam's thermal insulation, compression performance, hydrophobicity, and flame-retardancy were comprehensively assessed to validate the superior multifunctional properties of the microcellular H-PVDF foam. This study realized the fabrication of H-PVDF foams with significant potential applications and represent the first systematic investigation into the foaming performance of H-PVDF.

## EXPERIMENTAL

### Materials

Ultra-high molecular weight poly(vinylidene fluoride) (H-PVDF), Kynar® HSV 900, in powder form, with a density of 1.78 g/cm<sup>3</sup>, was obtained from Arkema Inc., France. This polymer exhibited a melt viscosity of about 50 kPoise (measured at 100 s<sup>-1</sup> *via* ASTM D3835 at 232 °C), a melt temperature of 167 °C. It was a mixture of two components with different molecular weights: 1,367 kDa and 92,840 kDa.<sup>[31]</sup> Carbon dioxide (CO<sub>2</sub>) with a purity of 99.9%, was used as blowing agent for the microcellular foaming experiments, provided by Deyang Gas Company, China. *N,N*-dimethylformamide (DMF) with a purity of 99.5% was employed as solvent, obtained from Fuyu Chemical Reagent Factory, China.

### Foaming Sample Preparation

The preparation of the PVDF foams involved a two-step process: solvent casting and microcellular foaming. The schematic of the fabrication process is illustrated in Fig. 1. In the solvent casting stage, 20 g of PVDF powder was dissolved in 250 mL of DMF at 60 °C. A mechanical stirrer operating at 180 r/min for 3 h was employed to ensure thorough dissolution and uniform dispersion of the polymer. Then, the viscous solution was placed in a blast drying oven at 80 °C for 10 h to allow complete solvent evaporation. To ensure total volatilization of the solvent, the PVDF sheet was stabilized in the oven at 160 °C for 5 h. The sheet was subsequently cut into bulk form with dimensions of 12 mm × 4 mm × 2 mm to be used in the supercritical CO<sub>2</sub> (scCO<sub>2</sub>) foaming process.

During the foaming phase, batch foaming experiments were conducted using a self-designed high-pressure autoclave, which was equipped with a PID temperature control system and a plunger pump (260D, TELEDYNE, USA). First, the sealed autoclave, containing solid PVDF, was heated to the desired foaming temperature. Then, a 20-min scCO<sub>2</sub> saturation process was performed to achieve a homogeneous mixture of the PVDF matrix and CO<sub>2</sub> molecules. Next, the foaming process was triggered by a rapid depressurization of the autoclave. Finally, the PVDF foam sample was cooled in a water bath to stabilize the cell structure. Four pressure levels (6.9, 13.8, 21.7, and 27.6 MPa), were applied at foaming temperature between 150 and 220 °C.

### Characterization

The dynamic mechanical properties of PVDF were analyzed using a dynamic mechanical analyzer (DMA-850, TA Instruments, USA), equipped with a film tension clamp. A specimen with dimensions of 30 mm × 5 mm × 2 mm was subjected to heating from 20 °C to 250 °C at a rate of 3 °C/min, with a shearing frequency of 1 Hz and a strain of 1% during testing.

The crystallization behavior of solid H-PVDF and H-PVDF foams was examined using a differential scanning calorimeter (DSC 400, NETZSCH, Germany). Approximately 5–10 mg of each sample was encapsulated in an aluminum crucible, and heated from 30 °C to 220 °C at a heating rate of 10 °C/min. The samples were subsequently isothermally treated at 220 °C for 5 min to eliminate thermal history before being cooled to 30 °C at a cooling rate of 10 °C/min. Additionally, H-PVDF foams were subjected to a single heating cycle from 30 °C to 220 °C at a heating rate of 10 °C/min. According to the DSC data, the degree of crystallinity ( $X_c$ ) can be calculated as fol-

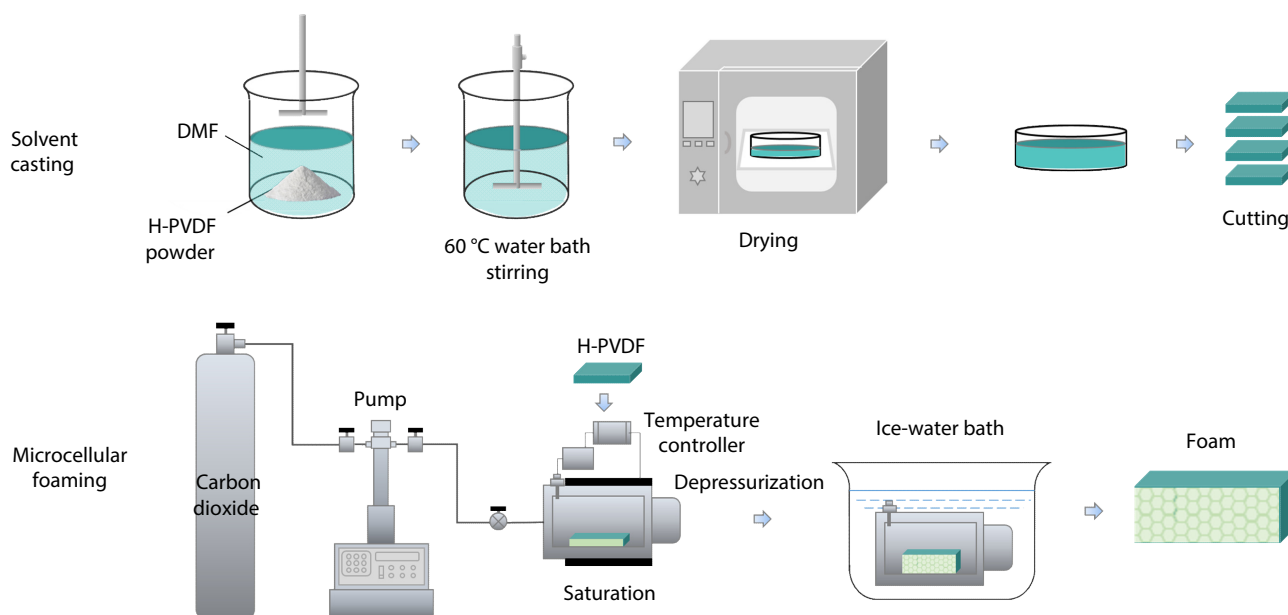


Fig. 1 The schematic diagram of the preparation process of H-PVDF microcellular foam.

lows:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

where  $\Delta H_m$  represent the melting enthalpy, and  $\Delta H_m^0$  is the theoretical melting enthalpy of PVDF, which is 105 J/g.<sup>[32]</sup> The non-isothermal crystallization of solid H-PVDF was investigated through a cooling process in which the sample was cooled at a rate of 10 °C/min from 250 °C to 30 °C, following a 5-min isothermal treatment to eliminate the thermal history. The non-isothermal crystallization kinetic was analyzed using the Jeziorny-modified Avrami model.<sup>[33]</sup> The Avrami equations, commonly used to describe the isothermal crystallization of polymers are given by:

$$1 - X_t = \exp(-Z_t t^n) \quad (2)$$

$$\ln[-\ln(1 - X_t)] = \ln Z_t + n \ln t \quad (3)$$

where  $X_t$  represents the relative degree of crystallinity at time  $t$ ,  $Z_t$  represents the crystallinity kinetic rate constant, and  $n$  is the Avrami exponent.

According to Eq. (3), the  $Z_t$  and  $n$  can be determined from the plot of  $\ln[-\ln(1 - X_t)]$  versus  $\ln t$ . The crystallization half-time ( $t_{1/2}$ ), defined as the time required for 50% crystallization, was calculated as:

$$t_{1/2} = (\ln 2 / Z_t)^{1/n} \quad (4)$$

For non-isothermal crystallization rate constant ( $Z_c$ ) was modified using the Jeziorny method:

$$\ln Z_c = \ln Z_t / v \quad (5)$$

where  $v$  refers to the cooling rate.

The densities of solid H-PVDF and H-PVDF foams ( $\rho_s$  and  $\rho_f$ , respectively), were measured using the water displacement method.<sup>[34]</sup> The expansion ratio ( $\varphi$ ) of the PVDF foam was determined as follows:

$$\varphi = \frac{\rho_s}{\rho_f} \quad (6)$$

The microcellular morphology of the fabricated PVDF foams was observed via scanning electron microscopy (SEM-30 Plus, COXEM Co., Ltd., Korea). After being immersed in liquid nitrogen for 1 h, the PVDF foam were fractured using pliers. To mitigate electrostatic charging during SEM analysis, the fractured surface were coated with a thin layer of platinum using a sputtering coater (ETD-900M, Elaborate Technology Development, China). The cell size and cell density of H-PVDF foams were quantified using Image-Pro Plus software. To ensure statistical accuracy, at least 200 cells were counted for each sample. The cell density ( $N_0$ ) could be calculated using the following equation:

$$N_0 = \varphi \left( \frac{n}{A} \right)^{3/2} \quad (7)$$

where  $n$  represents the number of cells, and  $A$  is the analyzed area.

The crystallographic structure of solid H-PVDF and H-PVDF foams were investigated using X-ray diffraction (D8 Advance, Bruker, Germany). An incident wavelength of 0.154 nm, a scanning angle range of 10°–45°, and a scanning speed of 3 (°)/min was set in the experiment. The working current and voltage were 150 mA and 40 kV, respectively. The samples were stored at ambient conditions for 10 days before testing. According to the curve deconvolution technique, the XRD patterns were fitted to evaluate the crystallinity of PVDF.<sup>[35]</sup> The total crystallinity ( $\varphi_{\text{total}}$ ) and the  $\beta$ -phase crystallinity ( $\varphi_\beta$ ) were calculated by following equations:

$$\varphi_{\text{total}} = \left( \frac{\sum A_{\text{crys}}}{\sum A_{\text{amr}} + \sum A_{\text{crys}}} \right) \times 100\% \quad (8)$$

$$\varphi_\beta = \frac{\sum A_\beta}{\sum A_\alpha + \sum A_\beta} \times \varphi_{\text{total}} \times 100\% \quad (9)$$

where  $\sum A_{\text{crys}}$  and  $\sum A_{\text{amr}}$  are the total integrated areas of crystalline and amorphous peaks, respectively.  $\sum A_\alpha$  and  $\sum A_\beta$

represent the total integrated areas from the  $\alpha$ - and  $\beta$ -phase peaks, respectively.

### Properties Testing

The thermal insulation properties of H-PVDF foams with varying expansion ratios were assessed using an infrared thermal imaging camera (ST9450, Smart sensor Co., Ltd., China). The samples were placed on a hot platform at 80 °C for 5 min to reach thermal equilibrium, before recording the temperature. The thermal conductivity of H-PVDF foams was determined using a thermal constant analyzer (TPS-2500S, Hot Disk, Sweden), with solid H-PVDF tested for comparison. A Kapton sensor with a 4 mm diameter was employed to supply heat and simultaneously recorded temperature variation. Two cuboid samples with dimensions of 8 mm × 6 mm × 6 mm were used for testing.

The compressive properties of H-PVDF foams were investigated using a universal testing machine (HDW-2000, Hengxu, China) at a compression rate of 1 mm/s. Cubic H-PVDF foams with dimensions of 6 mm × 6 mm × 6 mm were tested at least three times, and the average value was recorded.

To assess the hydrophobic properties of solid H-PVDF and H-PVDF foams, the water contact angle testing was conducted using a contact angle tester (JC 2000D, Powereach, China) with deionized water as probe liquid. Each sample was tested three times at different locations and the averaged value was recorded.

The flame-retardant property of H-PVDF foams was verified by a combustion testing using an alcohol lamp. The cubic foam with an expansion ratio of 40-fold and dimensions of 4 mm × 11 mm × 20 mm was used for testing. The limiting oxygen index (LOI) of solid H-PVDF and H-PVDF foams with varying expansion ratios was determined using an automated oxygen index instrument (JF-5, Air Time Co., Ltd., China), according to GB/T2406.2-2009.<sup>[36]</sup>

## RESULTS AND DISCUSSION

### Thermal and Crystallization Behavior of PVDF

The thermodynamic behavior of polymers has a crucial influence in their foaming performance. Fig. 2 presents the DSC and DMA test results of H-PVDF. Additionally, to compare the effect of molecular weight on the thermodynamic behavior of PVDF, low molecular weight PVDF (L-PVDF, Kynar®720, from Arkema, with a molecular weight of approximately  $2 \times 10^5$ ) was tested under identical experimental conditions. Fig. 2(a) shows the curves of storage modulus ( $G'$ ) as a function of temperature for H-PVDF and L-PVDF. In the temperature range of 100–170 °C, both H-PVDF and L-PVDF exhibit a gradual decrease in  $G'$  as the temperature increases. This decline is attributed to the weakening of intermolecular forces between polymer chains and the corresponding increase in their mobility. Between 170–190 °C, the rapid decrease in  $G'$  is due to the melting of crystals, which is consistent with the crystallization behavior shown in the DSC melting thermogram (Fig. 2b). At this stage, the entangled network in the H-PVDF melt results in a much slower decrease in  $G'$  compared to L-PVDF. Notably, above 190 °C,  $G'$  of H-PVDF remains stable at  $10^6$  Pa, while  $G'$  of L-PVDF decreases to below  $10^5$  Pa. The melt strength of the polymer is typically associated with its storage modulus. It indicates that the melt strength of H-PVDF can maintain a relatively high level at elevated temperatures.<sup>[37]</sup>

Figs. 2(b) and 2(c) show the DSC thermograms of H-PVDF and L-PVDF during the heating and cooling stages. While both H-PVDF and L-PVDF exhibit pronounced crystallization behavior, H-PVDF demonstrates delayed and weakened crystallization. As shown in Table 1, compared to L-PVDF, H-PVDF exhibits a lower melting peak ( $T_m$ ), a broader melting range ( $\Delta T_m$ ), and a lower melting enthalpy ( $\Delta H_m$ ). Fig. 2(d) presents

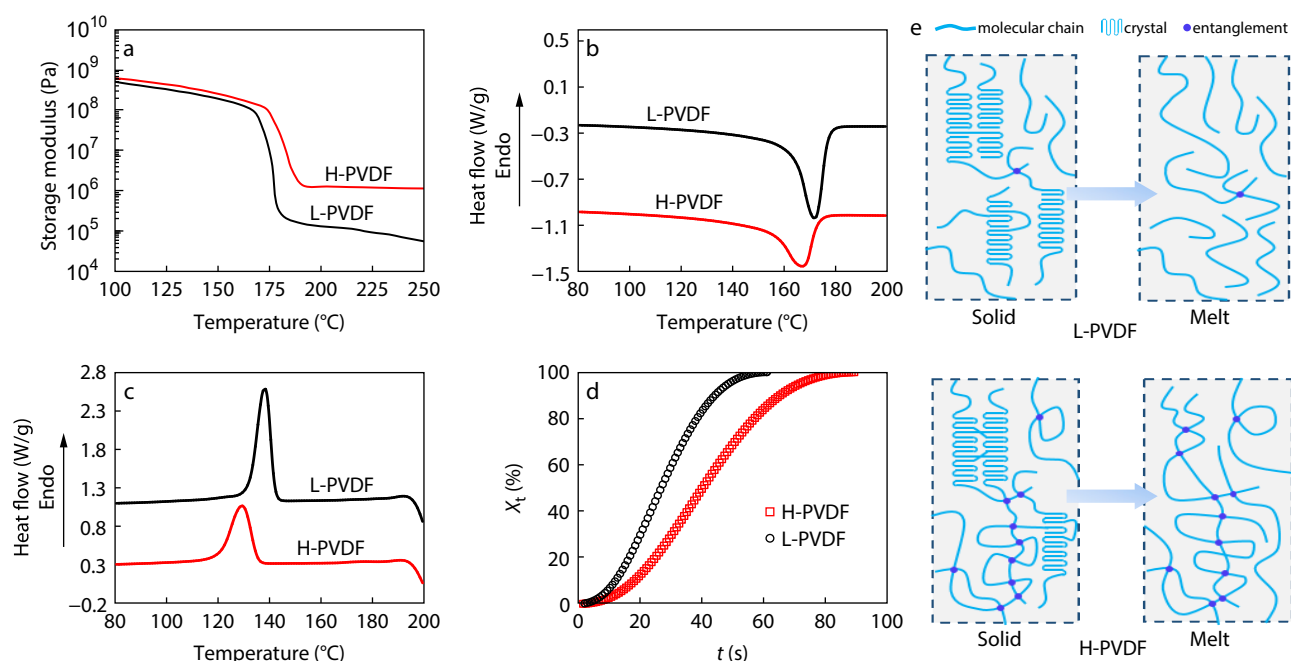


**Fig. 2** (a) Storage modulus curves of H-PVDF and L-PVDF as a function of temperature. DSC thermograms of H-PVDF and L-PVDF during the (b) heating stage, and (c) cooling stage. (d) Relative crystallinity curves of H-PVDF and L-PVDF as a function of time. (e) Schematic illustration of the molecular chain behavior of H-PVDF and L-PVDF during melting.

**Table 1** The melting and crystallization behaviors of H-PVDF and L-PVDF.

|        | Melting range<br>( $\Delta T_m$ , °C) | Melting peak<br>( $T_m$ , °C) | Melting enthalpy<br>( $\Delta H_m$ , J/g) | Crystallization<br>range (°C) | Crystallization<br>peak (°C) | Crystallization<br>enthalpy (J/g) |
|--------|---------------------------------------|-------------------------------|-------------------------------------------|-------------------------------|------------------------------|-----------------------------------|
| H-PVDF | 154.8–173.3                           | 167.0                         | 55.4                                      | 120.9–135.5                   | 129.3                        | 46.1                              |
| L-PVDF | 163.3–177.3                           | 171.9                         | 72.8                                      | 132.2–142.2                   | 138.2                        | 65.3                              |

the non-isothermal crystallization kinetics of H-PVDF and L-PVDF. The relative crystallinity ( $X_t$ ) curves as a function of time for H-PVDF and L-PVDF show an S-shaped, with the curve for H-PVDF shifted to the right and having a lower slope. As shown in Table 2, compared to L-PVDF, H-PVDF exhibits an extended crystallization half-time ( $t_{1/2}$ ) increasing from 29.1 s to 39.8 s, and a reduced non-isothermal crystallization rate constant ( $Z_c$ ) from  $4 \times 10^{-23}$  to  $1 \times 10^{-24}$ . This behavior is attributed to the reduced chain mobility of H-PVDF result from its ultra-high molecular weight, which suppresses crystallization and diminishes crystal integrity.<sup>[38]</sup> Furthermore, the Avrami exponents of H-PVDF and L-PVDF are very close, indicating that L-PVDF and H-PVDF have similar crystal growth dimensions.<sup>[39]</sup> Notably, the slow crystallization behavior of H-PVDF helps to suppress abrupt change in storage modulus, as shown in Fig. 2(a). The slow crystallization behavior can provide extended time for cell growth, which facilitates the production of foam with a higher expansion ratio.

**Table 2** The non-isothermal crystallization kinetic of H-PVDF and L-PVDF.

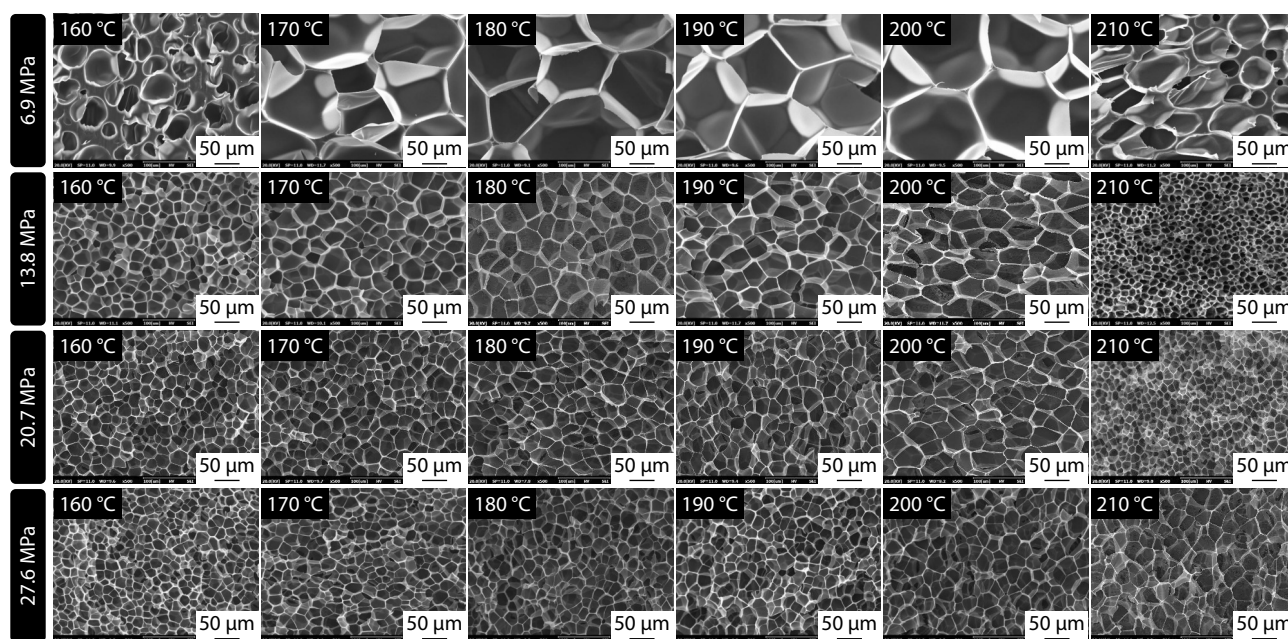
|        | $n$  | $Z_t$                | $Z_c$               | $t_{1/2}$ (s) |
|--------|------|----------------------|---------------------|---------------|
| L-PVDF | 2.44 | $1.9 \times 10^{-4}$ | $4 \times 10^{-23}$ | 29.1          |
| H-PVDF | 2.40 | $1.0 \times 10^{-4}$ | $1 \times 10^{-24}$ | 39.8          |

Fig. 2(e) illustrates the melting mechanisms of H-PVDF and L-PVDF. Despite having a lower crystallinity, the entangled network of H-PVDF results in a storage modulus comparable to that of L-PVDF at solid state, as shown in Fig. 2(a). After

melting, compared to L-PVDF, H-PVDF exhibits a significant amount of entanglements and stronger molecular chain interactions. As a result, H-PVDF maintains a high melt strength over a wide temperature range, even above its melting temperature, which can effectively prevent gas escape during the foaming process. This exceptional melt strength is markedly different from semi-crystalline polymers with low molecular weights.<sup>[40,41]</sup>

### Foaming Behavior of PVDF

Fig. 3 presents representative SEM images of the cellular morphology of H-PVDF foams prepared under different saturation pressures and foaming temperatures. These images indicate that nearly all foams exhibit highly uniform cell structures, suggesting that H-PVDF has excellent foaming properties. Fig. 4 shows the variation of cell size and cell density as a function of temperature at different saturation pressures. It is evident that saturation pressure has a significant effect on the foam cell structure. Specifically, cell density increases from  $10^7$  cells/cm<sup>3</sup> to  $10^{10}$  cells/cm<sup>3</sup> as the pressure rises from 6.9 MPa to 27.6 MPa, indicating that higher saturation pressure results in a denser cellular morphology. This phenomenon can be attributed to the enhanced gas solubility and intensified CO<sub>2</sub> plasticization effect at higher pressures. This can increase the nucleation driving force while reducing the elastic energy barrier in cell nucleation process, thus promoting a higher cell density. Simultaneously, cell size decreases from approximately 60  $\mu$ m at 6.9 MPa to about 10  $\mu$ m at 27.6 MPa. This suggests that the increase in cell density caused by high saturation pressure suppresses cell growth, leading to finer cell sizes.<sup>[42]</sup> At a constant pressure, cell

**Fig. 3** SEM images of the H-PVDF foams prepared under different temperatures and pressures.

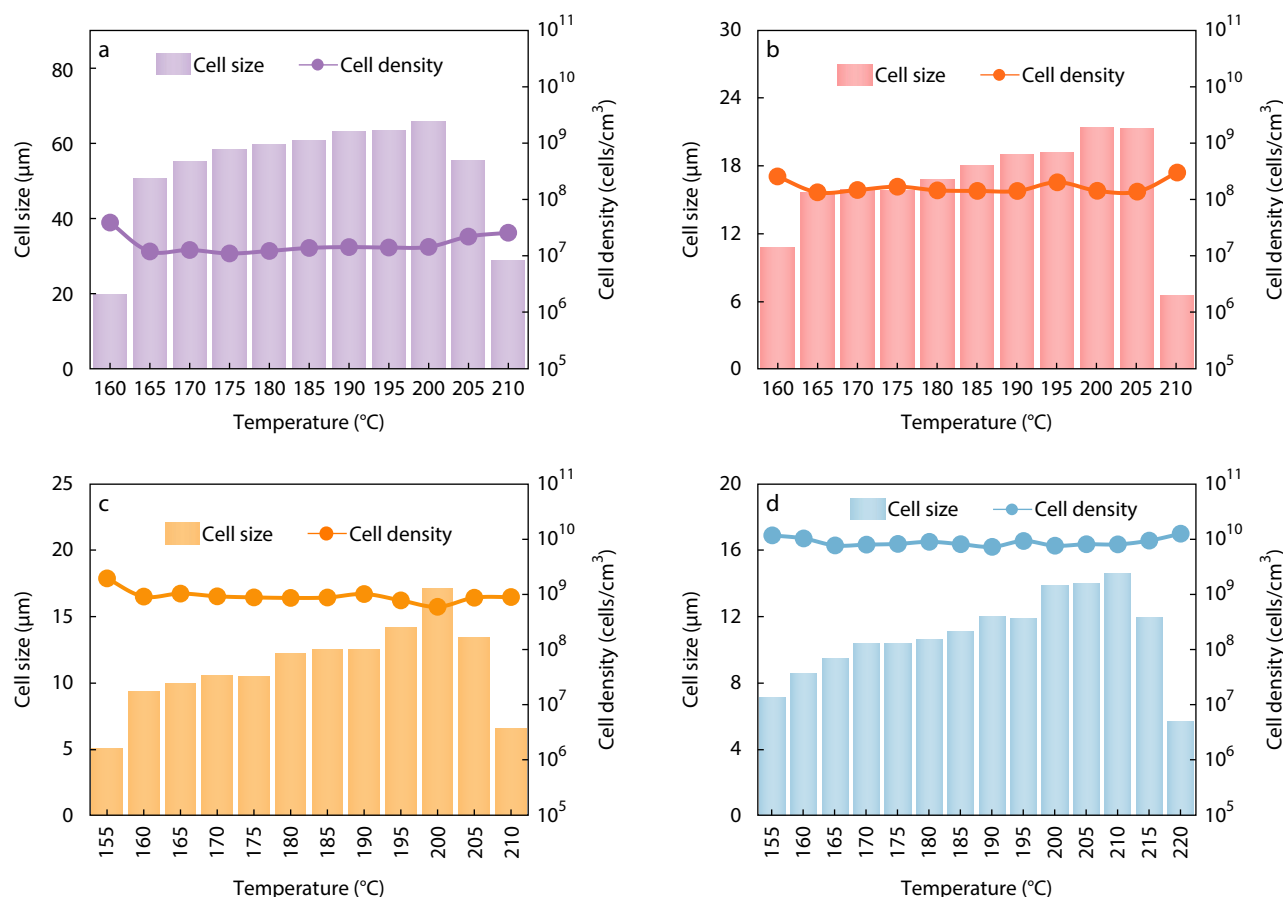


**Fig. 4** Cell size and cell density as a function of foaming temperature under saturation pressure of (a) 6.9 MPa, (b) 13.8 MPa, (c) 20.7 MPa and (d) 27.6 MPa.

density remains relatively stable, while cell size shows noticeable variation with temperature. As the foaming temperature increases, cell size initially increases and then decreases. In the temperature range of 150–175 °C, the reduction in the resistance to cell growth caused by the gradual melting of crystalline regions promotes an increase in cell size. In 175–205 °C, the mobility of the molecular chains decreases with the temperature increases, thereby reducing the resistance to growth. Furthermore, at elevated temperatures, H-PVDF melt maintains stable melt strength for an extended duration prior to solidification. This can provide more time for cell growth and further promote an increase in cell size. However, when the temperature exceeds 205 °C, the weakened melt strength caused by excessive temperature leads to cell shrinkage and a noticeable reduction in cell size.

Fig. 5(a) illustrates the dependence of the expansion ratio of H-PVDF foams on the foaming temperatures at different saturation pressures. The expansion ratio initially increases and then decreases with increasing foaming temperature. The foam prepared at 210 °C and 27.6 MPa saturation pressure exhibits the highest expansion ratio, reaching 55.6-fold, an unprecedented value for PVDF foams. To further evaluate the impact of saturation pressure on foaming behavior, we propose defining the foaming temperature window as the temperature range within which the expansion ratio exceeds 10-fold. The foaming temperature range and optimal expan-

sion ratio at different pressure are derived from Fig. 5(b). As the pressure increases from 6.9 MPa to 27.6 MPa, the foaming temperature window for H-PVDF foams expands significantly from 35 °C to 65 °C, while the optimal expansion ratio increases dramatically from 20.6-fold to 55.6-fold. The ultra-high expansion ratio of H-PVDF foams can be attributed to the following reasons. Firstly, ultra-high molecular weight PVDF has extremely high melt strength, which can avoid cell rupture and collapse even at temperatures much higher than its melting temperature, which expands the foaming temperature window. Moreover, such a high foaming pressure of 27.6 MPa provides sufficient driving forces and gases for cell growth.

Fig. 5(c) presents a chromatogram showing the foaming temperature range and expansion ratios for pure PVDF foams prepared at 13.8 MPa in recent studies.<sup>[25,39,43,44]</sup> In this figure, individual chromatographic columns represent the results of each study, with the X-axis representing the foaming temperature, and color gradients denoting the corresponding expansion ratios. Compared to previous studies, the foam produced in this work exhibits the largest colored region and the most intense red coloration on the chromatographic column, indicating the broadest foaming temperature range and the highest expansion ratio of H-PVDF foams, respectively. These superior structural characteristics highlight the increased structural, performance, and application advantages of H-PVDF in advanced functional foam applications.

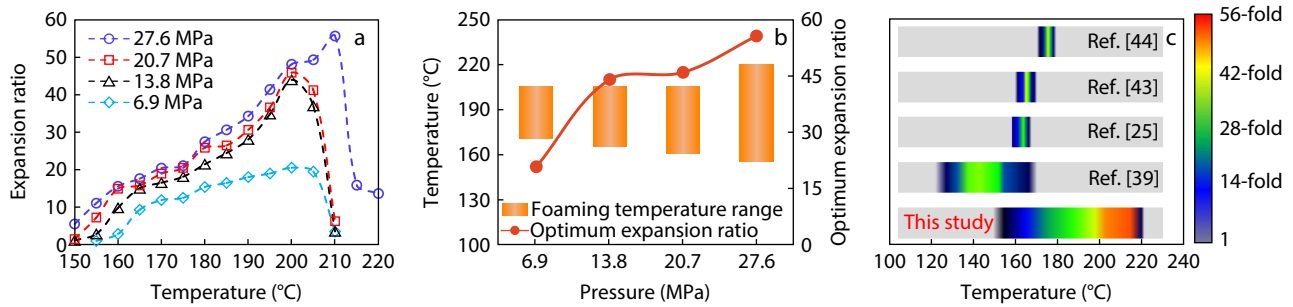


**Fig. 5** (a) Expansion ratio of PVDF foams as a function of foaming temperature under saturation pressures of 6.9, 13.8, 20.7, and 27.6 MPa. (b) Foaming temperature range and optimal expansion ratios of H-PVDF under different saturation pressures. (c) Comparison of expansion ratios at various foaming temperatures between this and previously reported studies.

### Crystallization Analysis of PVDF Foams

Microcellular foaming has significant influences on the crystallization behavior of polymers. Fig. 6 presents the DSC thermograms and XRD spectra of solid H-PVDF and H-PVDF foams. As shown in Figs. 6(a) and 6(b), H-PVDF foams exhibit distinct double melting peaks, in contrast to solid H-PVDF, indicating a bimodal crystallization phenomenon during the foaming process.<sup>[45]</sup> Notably, the high-temperature melting peak of H-PVDF foam aligns with that of solid H-PVDF, but its area gradually reduces with increasing temperature or pressure, while the low-temperature melting peaks shifts to high temperature. The high-temperature melting peak corresponds to the unmelted crystalline regions in solid H-PVDF. As the molecular chain mobility increases with temperature or pressure, the integrity of crystals formed during the foaming process is enhanced, thereby shifting the low-temperature melting peak to higher values. These observations confirm the significant impact of foaming conditions on the crystallization within the PVDF matrix.

Promoting the formation of the  $\beta$ -phase in PVDF is of great interest due to its superior dielectric properties. The crystal-

lization behavior of H-PVDF foam was investigated through XRD. As shown in Figs. 6(c) and 6(d), while the overall crystallinity of H-PVDF foam remains relatively stable as the expansion ratio increases, the proportion of the  $\beta$ -phase gradually increases. Specifically, the diffraction peaks of the  $\alpha$ -phase at  $17.8^\circ$  (100),  $18.3^\circ$  (020), and  $26.6^\circ$  (021) gradually diminish, whereas the characteristic diffraction peak of the  $\beta$ -phase at  $20.6^\circ$  (corresponding to the (200/110)) becomes more pronounced. This phenomenon is likely attributed to the stretching of polymer chains and the high cooling rate during foaming process, which promotes the formation of the  $\beta$ -phase.<sup>[46,47]</sup> Furthermore, in Figs. 6(e) and 6(f), for a given expansion ratio, H-PVDF foams fabricated above the melting temperature ( $T_m$ ) exhibits higher crystallinity and a larger proportion of the  $\beta$ -phase than the foam fabricated below  $T_m$ . When the foaming temperature ( $T_f$ ) exceeds  $T_m$ , the increased degree of supercooling and the absence of the residual  $\alpha$ -phase crystals in the melt promote the generation of  $\beta$ -phase crystals during the foaming process. These findings provide a fundamental strategy for regulating the micro-

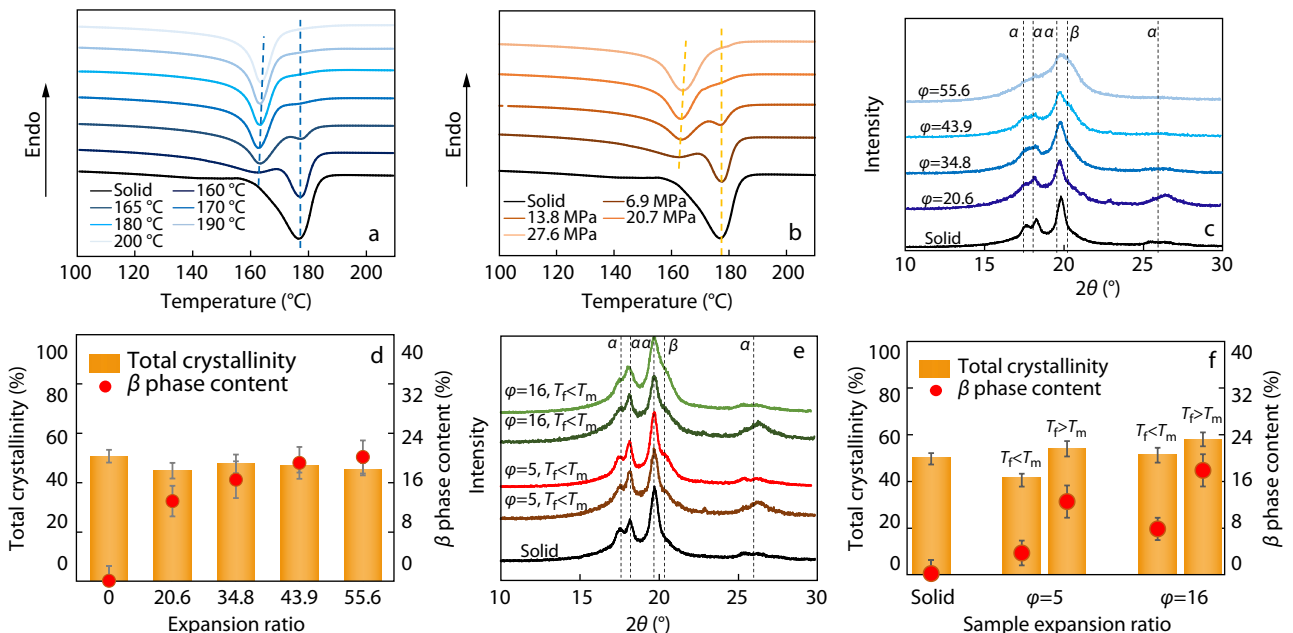


**Fig. 6** DSC curves of the solid PVDF and PVDF foams at (a) the same saturation pressure and (b) the same foaming temperature. (c) XRD patterns and (d) total crystallization and  $\beta$  phase content of the solid H-PVDF and H-PVDF foams with different expansion ratio. (e) XRD patterns and (f) total crystallization and  $\beta$  phase content of the H-PVDF samples with same expansion ratio but different foaming temperature ( $T_f$ ).

phase structure of H-PVDF foam, thereby broadening its potential applications in piezoelectric or ferroelectric fields.

### Thermally Insulating Performance of PVDF Foams

Microcellular polymer foams play a pivotal role in thermal insulation applications. In this study, the thermal insulation performance and underlying mechanisms of H-PVDF foams were systematically investigated through comprehensive characterization. Fig. 7(a) presents infrared thermographic images of H-PVDF foams after reaching thermal equilibrium on an 80 °C hot plate for 5 min. As the expansion ratio increases from 21.5-fold to 55.6-fold, the surface temperature of the foams decreases from 36.6 °C to 34.5 °C. This demonstrates that thermal insulation performance of H-PVDF foams is related to their expansion ratio. Fig. 7(b) illustrates the relationship between thermal conductivity and expansion ratios in H-PVDF foams. With increasing expansion ratio, the thermal conductivity gradually decreases from 36.1 mW·m<sup>-1</sup>·K<sup>-1</sup> to 31.8 mW·m<sup>-1</sup>·K<sup>-1</sup>. According to classical heat transfer theory, heat convection in H-PVDF foams can

be neglected due to their micrometer-sized cell, which are significantly smaller than the mean free path of gas molecules. Consequently, heat transfer in H-PVDF foam is primarily governed by three mechanisms: solid-phase heat conduction ( $\lambda_{\text{sol}}$ ), gas-phase heat conduction ( $\lambda_{\text{gas}}$ ), and radiative heat conduction ( $\lambda_{\text{rad}}$ ), as depicted in Fig. 7(c).<sup>[34]</sup> These mechanisms can be described as follows:

$$\lambda = \lambda_{\text{sol}} + \lambda_{\text{gas}} + \lambda_{\text{rad}} \quad (10)$$

where  $\lambda_{\text{sol}}$  and  $\lambda_{\text{gas}}$  are influenced by the structure characteristics of the H-PVDF foam. Using Glickman's mathematic model for solid- and gas-phase heat transfer, the contributions can be calculated as follows:

$$\lambda_{\text{gas}} + \lambda_{\text{sol}} = \varepsilon k_{\text{gas}} + (1 - \varepsilon) \xi k_{\text{sol}} \quad (11)$$

$$\lambda_{\text{rad}} = \lambda - \lambda_{\text{gas}} - \lambda_{\text{sol}} \quad (12)$$

where  $\varepsilon$  represents the gas volume fraction in the H-PVDF foam,  $\xi$  is the tortuosity factor related to the foam's inherent irregular-

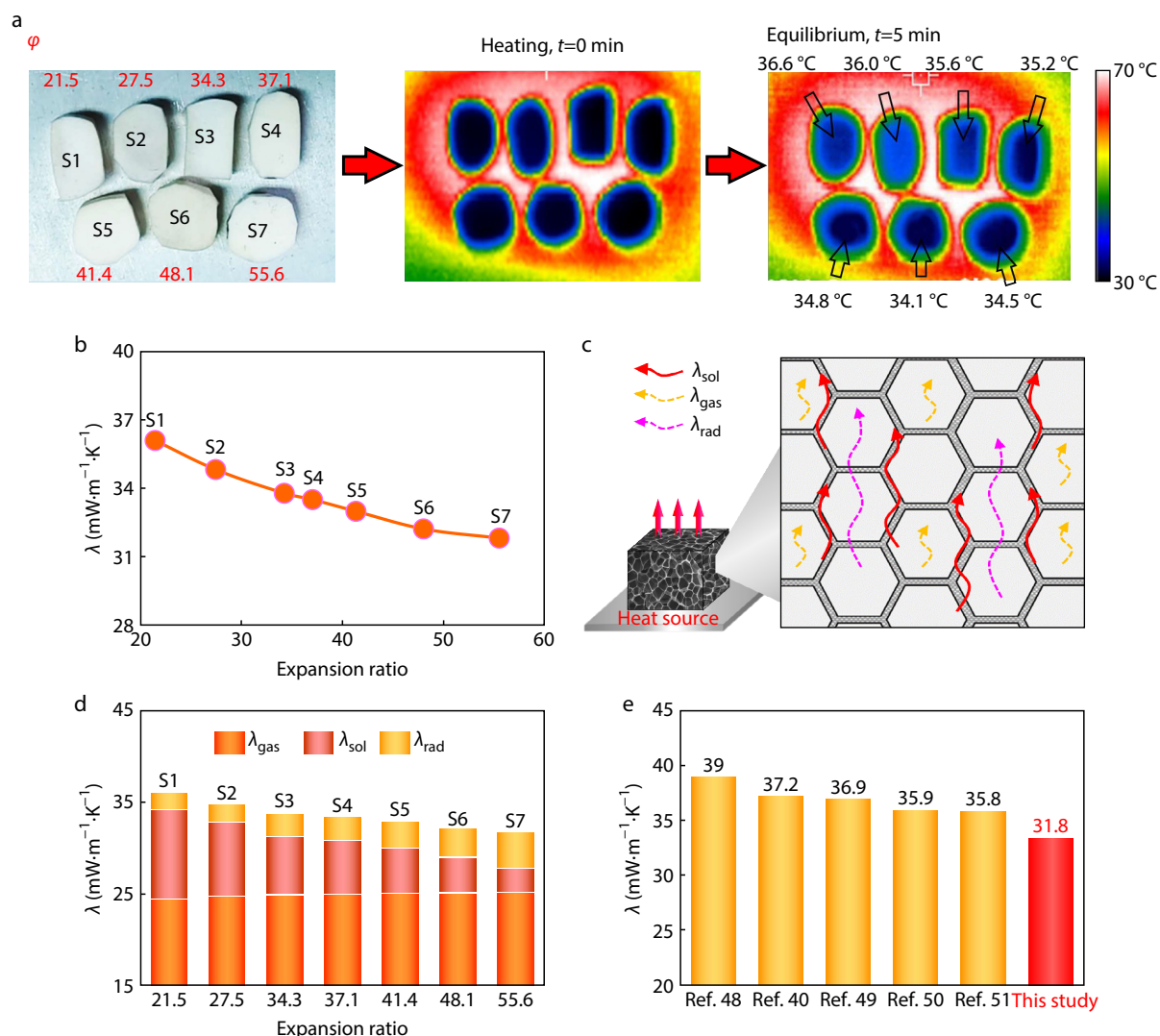


**Fig. 7** (a) Infrared thermographic images illustrating the thermal insulation performance of H-PVDF foams with different expansion ratios. (b) Measured total thermal conductivity of H-PVDF foams. (c) Schematic illustration of heat transfer mechanisms in H-PVDF foams. (d) Calculated thermal conductivities. (e) Comparison of H-PVDF foam thermal conductivity with values reported in previous studies.

ity, and  $k_{\text{sol}}$  and  $k_{\text{gas}}$  are the thermal conductivities of the solid and gas-phases, with measured values of 216.2 and 26.7  $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , respectively. As illustrated in Fig. 7(d), due to the inherently low thermal conductivity of the gas-phase and the high porosity of H-PVDF foam (ranging from 95.5% to 98.2%), the contribution of gas-phase heat conduction remains nearly constant across different expansion ratios. The observed reduction in thermal conductivity with increasing expansion ratio is attributed to the combined effects of decreased solid-phase heat conduction and increased radiative heat conduction. In addition to reducing the solid-phase thermal conduction, the decrease in the solid-phase fraction of the foam leads to an increase in radiative heat conduction. This is due to the higher reflectivity and lower infrared wave propagation speed of the polymer compared to air. Moreover, as the expansion ratio increases, thinner cell walls exacerbate thin-film interference, further enhancing radiative heat conduction.

Furthermore, as shown in Fig. 7(e), the H-PVDF foam prepared in this study exhibits the lowest thermal conductivity among several representative polymer foams reported in the literature.<sup>[40,48–51]</sup> This finding highlights the superior thermal insulation performance of ultra-high expansion ratio H-PVDF foam, underscoring its potential for advanced insulation applications.

### Mechanical Properties of PVDF Foams

Mechanical property is crucial for practical application of polymer foams. Fig. 8 shows the compressive properties of H-PVDF foams with varying expansion ratios and a nearly constant cell

size (approximately 11  $\mu\text{m}$ ). As seen in Fig. 8(a), the stress-strain curves of H-PVDF foam exhibit four characteristic stages during compressive testing: elasticity, post-peaking, stress plateau, and densification. In the elasticity stage, stress increases linearly with strain, indicating that H-PVDF foams undergo elastic deformation, primarily controlled by the elastic bending of the cell walls and cell skeleton. The modulus and strength are determined in this stage, which is critical performance parameters for H-PVDF foam. The second stage, called post-peaking stage, is associated with plastic bending of the foam structure. The stress plateau stage, occurring after yielding, represents the gradual collapse of the cell walls. In the final densification stage, the stress increases rapidly with strain, indicating the collapse of most of the cell skeleton and contact between opposing cell walls.

From Fig. 8(b), it can be observed that as the expansion ratio increases from 9.9-fold to 36.6-fold, the modulus decreases from 51.8 MPa to 3.1 MPa, and the strength decreases from 2.16 MPa to 0.28 MPa. According to the Gibson-Ashby theory, the compressive strength ( $\sigma_{\text{pl}}$ ) of the foam during the elasticity stage can be calculated as follows:<sup>[52]</sup>

$$\sigma_{\text{pl}} \approx \sigma_{\text{ys}} \left[ 0.3 \left( \frac{\zeta}{\varphi} \right)^{3/2} + 0.4 \frac{(1-\zeta)}{\varphi} \right] \quad (13)$$

where  $\sigma_{\text{ys}}$  represents the compressive strength of the solid polymer (the measured as 92 MPa for solid H-PVDF in this study).  $\zeta$  and  $(1-\zeta)$  represent the ratios of the cell skeleton and cell wall in the foamed polymer, respectively. The value of  $\zeta$  is selected within the range of 0–1 based on the cell structure of foams. According to the Gibson-Ashby model, the compressive

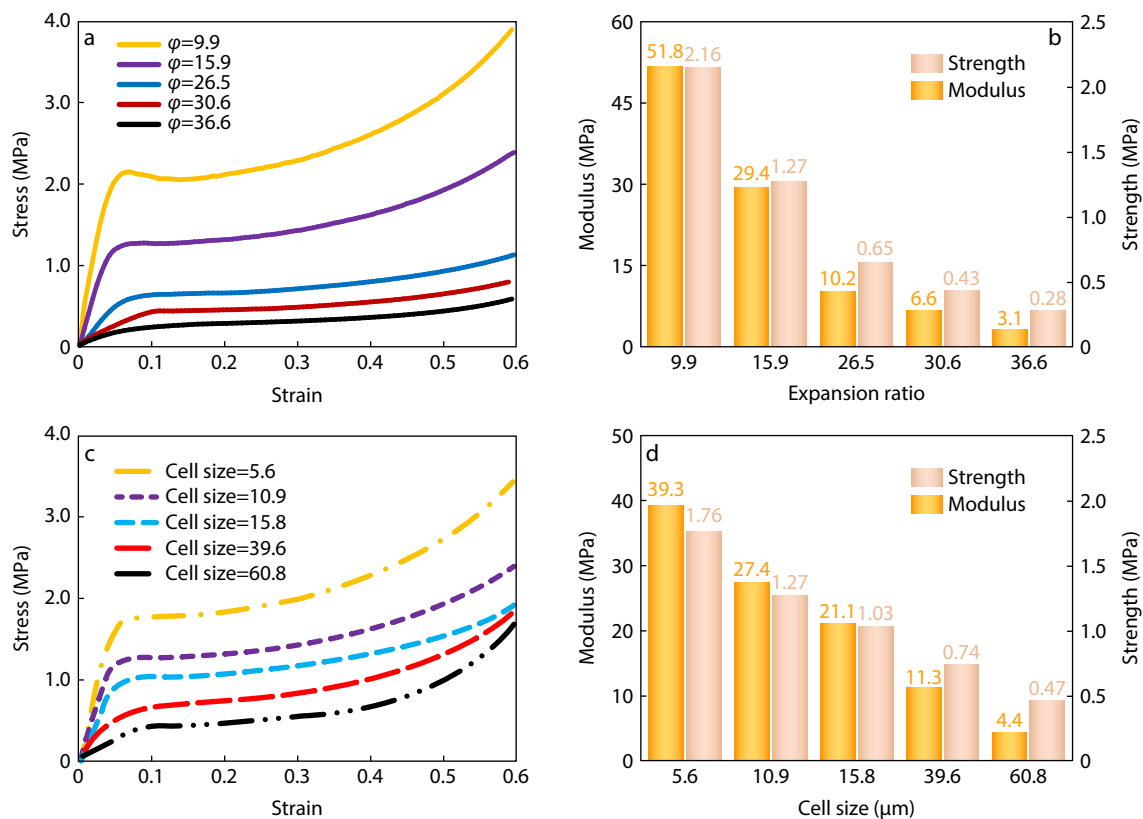


**Fig. 8** (a) Compressive stress–strain curves and (b) corresponding compressive modulus and strength of H-PVDF foams with identical cell sizes. (c) Compressive stress–strain curves and (d) compressive modulus and strength of H-PVDF foams with identical expansion ratios.

property of polymer foams could attribute to the cell skeleton and cell size.

Fig. 8(c) presents stress-strain curves of H-PVDF foams with similar expansion ratios (approximately 16-fold) but different cell sizes. According to the data in Fig. 8(d), as the cell size increasing from 5.6  $\mu\text{m}$  to 60.8  $\mu\text{m}$ , the modulus decreases from 39.3 MPa to 4.4 MPa, while the strength decreases from 1.76 MPa to 0.47 MPa. Furthermore, the rate of decline in compressive strength diminishes as the cell size increases. To theoretically investigate the relationship between compressive strength and cell size, the following equation was employed:<sup>[53]</sup>

$$\sigma = 36PLD / (9\pi D^4 - 16bh^3) \quad (14)$$

where  $L$  and  $D$  represent the length and the outside diameter of the strut, respectively,  $P$  represents the fracture load. And  $b$  and  $h$  represent the base and height of the triangular hole with in the cell wall, respectively. It is evident that the foams with the same expansion ratio but small cell size could exhibit superior compressive property.

### Flame-retardancy and Hydrophobicity of PVDF Foams

Flame-retardancy is a crucial property of thermal insulation materials, ensuring safety in practical applications. Figs. 9(a)–9(c) illustrate the combustion behavior of H-PVDF foam when directly exposed to flames, and compare it with polyurethane (PU) and polystyrene (PS) foams. H-PVDF foam demonstrates exceptional flame-retardancy. When subjected to direct flame exposure, H-PVDF foam does not generate smoke or molten droplets, and exhibits excellent self-extinguishing performances. In contrast, PU and PS foams are highly flammable, characterized by rapid combustion, the release of black smoke, and the formation of molten droplets. These combustion behaviors intensify fire hazards and pose severe challenges for personnel evacuation and rescue operations. The flame-retardancy of H-PVDF foams can be further quantified using the limiting oxygen index (LOI) test. The LOI values of solid H-PVDF and H-PVDF foam are presented in Fig. 9(d). Solid H-PVDF exhibits an LOI value of 41.6 vol%, substantially exceeding the oxygen concentration in ambient air (approximately 20.9 vol%). Notably,

the LOI of H-PVDF foam increases with its expansion ratio. This enhancement is likely attributed to its porous structure, which suppresses heat transfer and reduces the participation of solid materials in combustion. Therefore, H-PVDF foam provides superior safety performance under thermal insulation conditions.

Hydrophobicity is another crucial property for thermal insulation materials, as moisture accumulation can degrade their thermal insulation performance. Fig. 10 shows the water contact angle of H-PVDF foams with various cellular structures. As shown in Figs. 10(a) and 10(c), all H-PVDF foams exhibit significantly higher water contact angles compared to solid H-PVDF, which has a contact angle of 89.4°. The contact angle increases from 119.4° to 133.8° as the expansion ratio increases from 15.9-fold to 36.6-fold. This increase is attributed to the cellular structure, which enhances the surface roughness and porosity, thereby effectively reducing the liquid-solid contact area. According to the Cassie-Baxter model, the contact angle ( $\theta$ ) of H-PVDF foams can be expressed by the following equation:<sup>[54]</sup>

$$\cos\theta = f_{LS}\cos\theta^* - f_{LG} = (1 - f_{LG})\cos\theta^* - f_{LG} \quad (15)$$

where  $f_{LS}$  and  $f_{LG}$  represent the fractional area of liquid-solid and liquid-gas interfaces, respectively. And  $\theta^*$  represents the water contact angle of solid H-PVDF. For H-PVDF foam,  $f_{LG}$  corresponds to the porosity of the foam. Consequently, an increase in expansion ratio can enhance the water contact angle of H-PVDF foam.

The effect of cell size on hydrophobicity is shown in Figs. 10(b) and 10(d). The contact angle correspondingly decreases from 125.5° to 106.6°, with the cell size increasing from 5.7  $\mu\text{m}$  to 59.6  $\mu\text{m}$ . This decrease is owing to the increased density of cell walls per unit area at smaller cell sizes, which provides better structural support for water droplets. Smaller cell size inhibits water penetration into micro voids and promotes the formation of spherical droplets, thereby increasing the apparent contact angle. These findings demonstrate that reducing cell size is an effective strategy for enhancing the hydrophobic properties of H-PVDF foams.

### CONCLUSIONS

Superlight H-PVDF foams with exceptional thermal insulation,

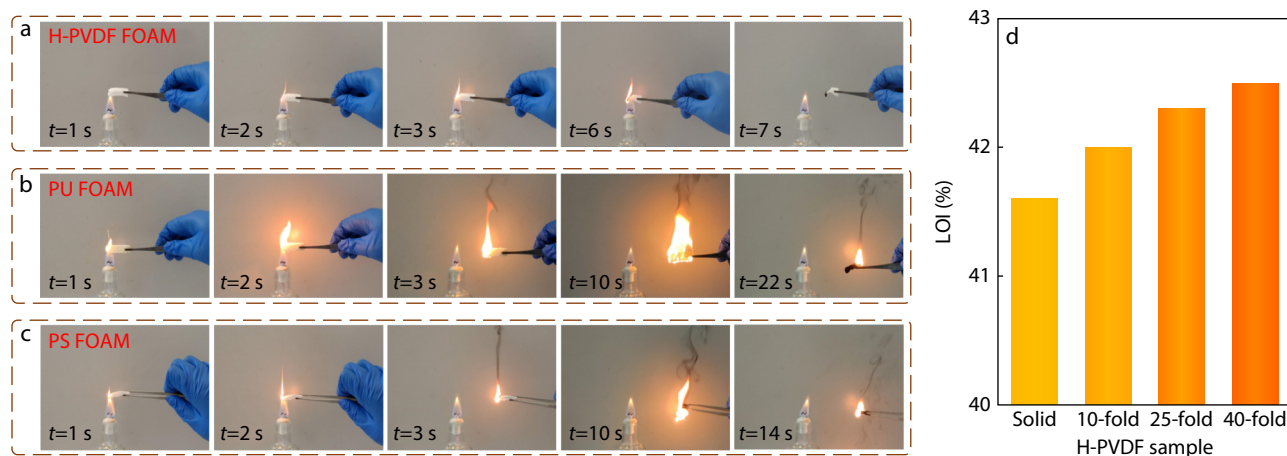


**Fig. 9** Representative images illustrating the combustion behaviors of various foams under direct flame exposure: (a) H-PVDF foam, (b) PU foam, and (c) PS foam. (d) Limiting oxygen index (LOI) values of solid H-PVDF and H-PVDF foams with different expansion ratios.

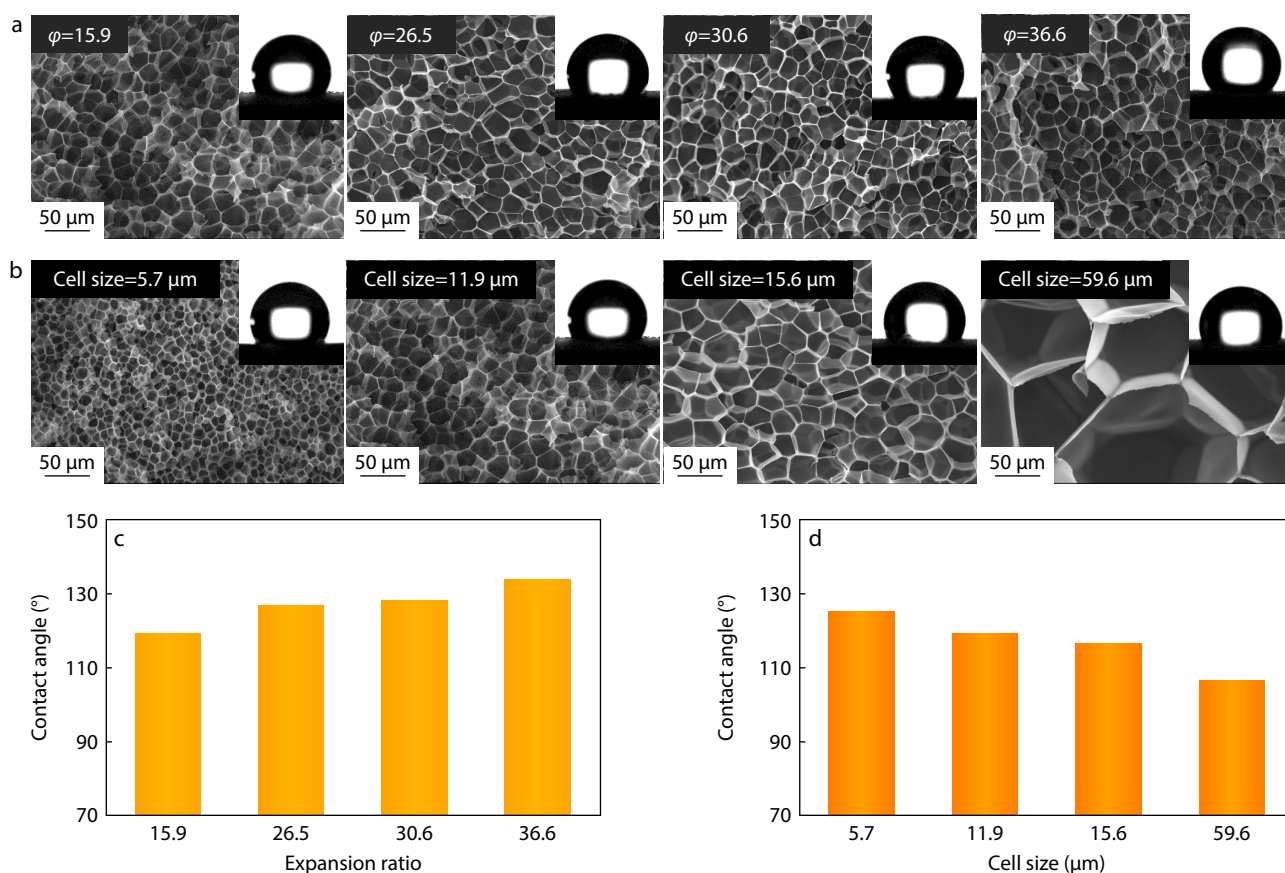


**Fig. 10** Images of cell morphology and water contact angles of H-PVDF foam with (a) same cell size and (b) same expansion ratio. Water contact angle values of H-PVDF foam with (c) different expansion ratios and (d) different cell sizes.

hydrophobicity, and flame-retardancy were successfully fabricated using  $\text{scCO}_2$  foaming technology. In this study, H-PVDF foams exhibited an unprecedented expansion ratio of 55.6-fold. The rheological and crystallization behavior characterization revealed that H-PVDF exhibits outstanding melt strength across a broad temperature range, even under condition of complete crystal melting. This remarkable characteristic is attributed to the enhanced intermolecular interactions and chain entanglements caused resulting from the ultra-high molecular weight of H-PVDF. This behavior is crucial for fabricating the ultra-high expansion ratio H-PVDF foam. By precisely controlling the foaming conditions, the expansion ratio can be systematically adjusted from 1.5-fold to 55.6-fold, corresponding cell size ranging from 10 μm to 60 μm. Crystallization analysis *via* XRD and DSC demonstrated that, at a given expansion ratio, foaming above the melt temperature preferentially induces the formation of the  $\beta$ -phase, in contrast to that foamed below melt temperature. This phenomenon can be attributed to the stretching effects under stress and the rapid temperature drop during foaming, which promotes the recrystallization of the molecular chains into the  $\beta$ -phase. The foam exhibits an exceptionally low thermal conductivity, measured of  $31.8 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at the expansion ratio of 55.6-fold. Furthermore, the foam demonstrates excellent performance, maintaining a high compressive strength of 0.27 MPa at 36.6-fold, while achieving a high LOI value of 42.5 vol% at 40-fold, ensuring outstanding flame-retardancy and self-extinguishing properties. The ultra-high expansion ratio also enhances hydrophobicity, with a water contact

angle of  $133.8^\circ$  at 36.6-fold. These exceptional properties, achieved through an environmentally sustainable foaming process, position the developed ultra-high expansion ratio H-PVDF foam as a highly promising candidate for thermal insulation applications in extreme environments.

### Conflict of Interests

The authors declare no interest conflict.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The author's contact information: guilong@sdu.edu.cn.

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