

# A 3D porous polymer film designed for efficient passive radiative cooling

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## ABSTRACT

Passive daytime radiative cooling (PDRC) technique can cool objects without energy consumption by reflecting sunlight and radiating heat into the cold outer space through atmospheric transparent windows (ATW). Here, 3D porous polydimethylsiloxane (P-PDMS) films with excellent radiative cooling properties were fabricated using citric acid monohydrate (CAM) templates. Integrating with high sunlight reflectance (78.6%) and great thermal emissivity (99.4%) in ATW, the test was performed in an outdoor environment with an average solar radiation of 715.09 W/m<sup>2</sup>. The maximum temperature of P-PDMS film is reduced to 15.4°C, and in the actual roof application test, P-PDMS film also show excellent passive radiant cooling performance of 8.3°C cooling in the house. The 3D-porous structure plays an important role in improving solar reflectivity and IR emissivity. Combined with efficient DRC capabilities and mass production compatibility, this work brings a new paradigm for the preparation of cooling devices with potential commercial applications in sustainable energy-free cooling.

## KEYWORDS

Passive radiative cooling; 3D Porous; Polydimethylsiloxane

## 1. INTRODUCTION

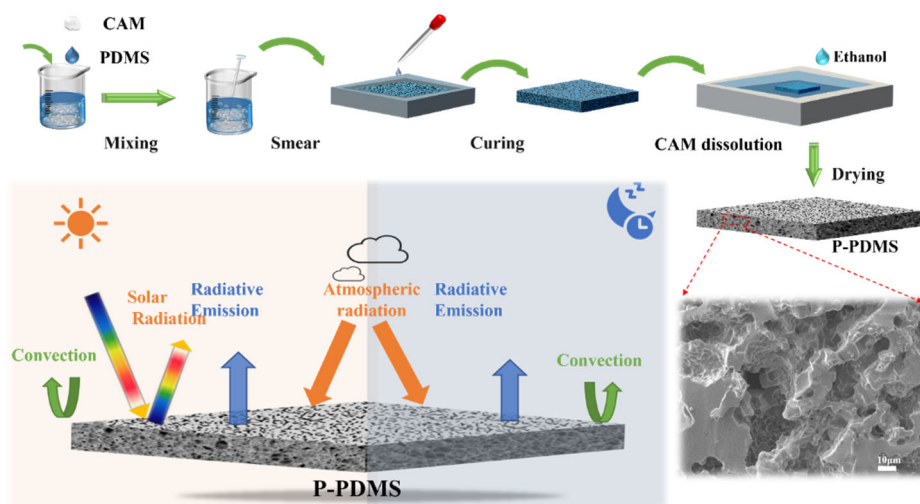
A Daytime radiative cooling (DRC) is an attractive technology that reduces ambient temperature with zero energy consumption[1]. In recent years, passive daytime radiative cooling composites and devices have become one of the research hotspots[2]. Polymer materials are widely used in daytime radiation cooling because of their low cost and are easy to make into different shapes. For example, Leroy et al. developed a sun-reflecting polyethylene aerogel (PEA)[3,4]. Feng et al. combined silica-polymethylpentene (TPX)[5,6] with ESR for applications in radiative refrigeration materials, among others. Among polymer materials, polydimethylsiloxane (PDMS) is an ideal candidate for DRC due to its transparency in the visible range and highly selective emission in the mid-infrared range[7,8]. The 3D porous polymer material significantly improves the reflectance in the sunlight band, while retaining the high radiation in the ATM band, which provides the possibility of obtaining low-cost and simple radiation cooling devices.

In this paper, we have presented a simple method to prepare 3D flexible porous emitters with excellent DRC properties. The experiment shows that the average temperature of P-PDMS film is 15.4°C lower than that of sub-environment when the average solar radiation is 715.09 W/m<sup>2</sup>. In the simulated house model test, it is found that the internal temperature of the house model covered with porous film decreases significantly, and the maximum temperature drop can reach 8.3°C. Combined with efficient DRC capabilities and large-scale production compatibility, this work brings a new paradigm to the preparation of cooling devices with potential commercial applications in sustainable energy-free cooling.

## 2. EXPERIMENTAL SECTION

### 2.1 Fabrication of porous P-PDMS films and T-PDMS films.

The preparation procedure of 3D Porous PDMS (P-PDMS) films has been shown in Fig. 1. Firstly, PDMS, N-hexane and curing agent were uniformly mixed at 10: 10: 1 mass ratio, and then CAM was added in the above solution and stirred at room temperature until the CAM dissolved. Subsequently, the PDMS and CAM solution with different mass ratios were obtained. Since the best radiation cooling ability, optical properties, and cooling effect of this film were obtained when the PDMS to CAM mass ratio was 1:1, this ratio was chosen for our later experiments.



**Figure 1.** Illustration of the fabrication of P-PDMS daytime radiative cooling film via a sacrifice template technique and photothermal management of P-PDMS film.

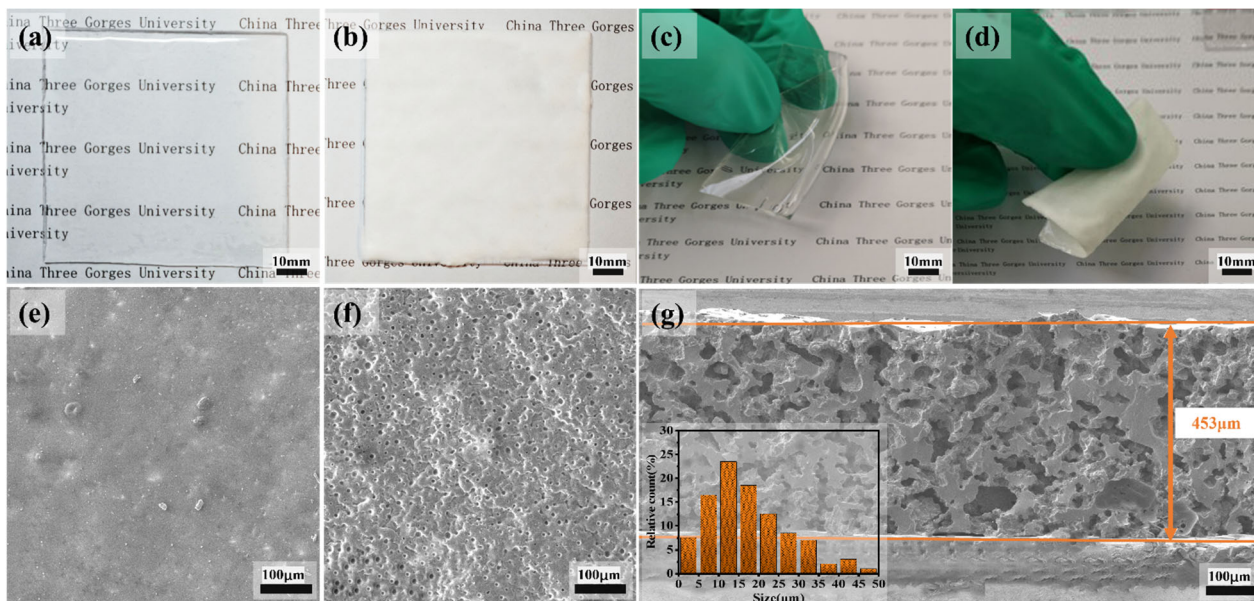
The precursor solution was debubbling by vacuum extraction before coated on a base plate by the dropper. After 2 hours drying in the oven at 80 °C, the cured P-PDMS was removed from the mold and then immersed in the ethanol solution for about 2 hours until the CAM was fully dissolved. Finally, a white P-PDMS film was obtained after solvent volatilization in the oven at 80 °C for 30 min. In the preparation process, the control sample transparent PDMS (T-PDMS) film was obtained without adding CAM and without immersion process.

## 3. RESULTS AND DISCUSSION

### 3.1 Structural Characteristics

As shown in Figs. 2a and 2b, after sacrificing the CAM template method, the transparent film is transformed into a porous PDMS film, which presents opacity. However, the flexibility is preserved with or without introducing CAM as found in Figs. 2c and 2d. Figs 2e and 2f show surface SEM images of the T-PDMS film and the P-PDMS film. The surface of the T-PDMS film is dense and flat,

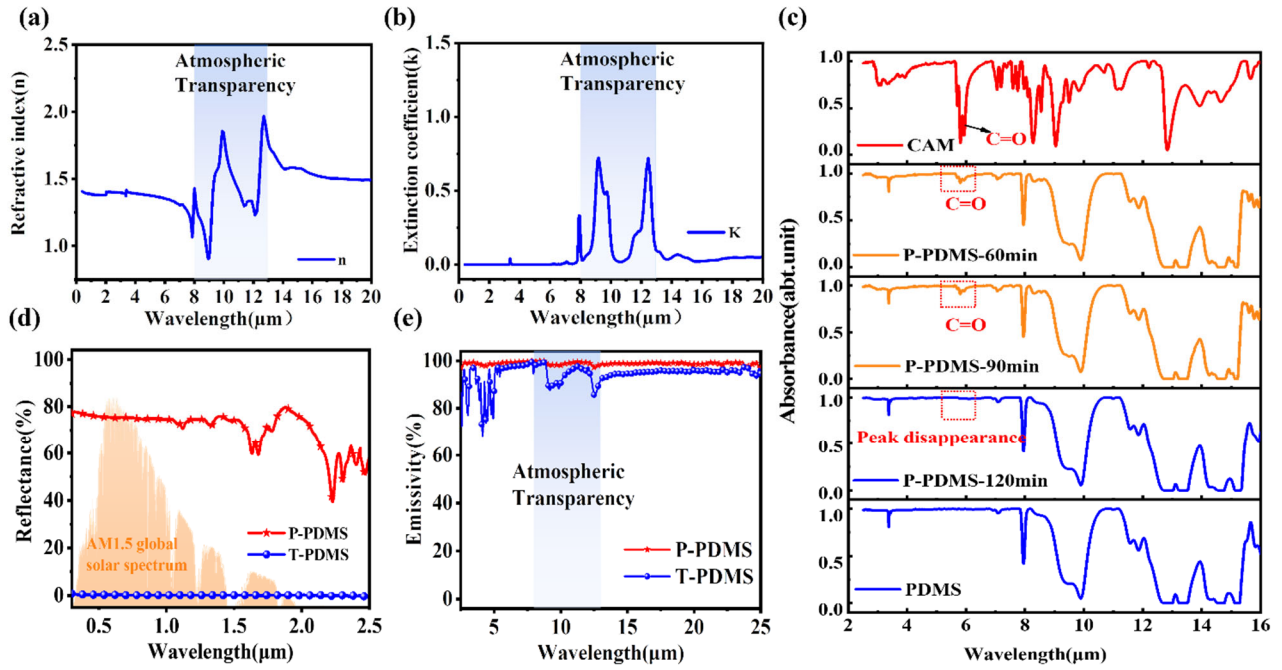
while the surface of the P-PDMS film is perforated. The cross-section image of P-PDMS film (Fig. 2g) shows a 3D interconnected hierarchical porous structure, and 68.5 % of the aperture was between 7.5  $\mu\text{m}$  and 22.5  $\mu\text{m}$  with the average aperture of 20.14  $\mu\text{m}$ .



**Figure 2.** Characterization of the P-PDMS and T-PDMS films. (a) Photograph of the T-PDMS film and (b) P-PDMS film. Photograph of the flexibilities of the (c) T-PDMS film and (d) P-PDMS film. SEM images of (e) T-PDMS film and (f) P-PDMS film. (g) SEM image of the cross-section of P-PDMS and Pore size distribution of the P-PDMS film.

### 3.2 Optical Properties

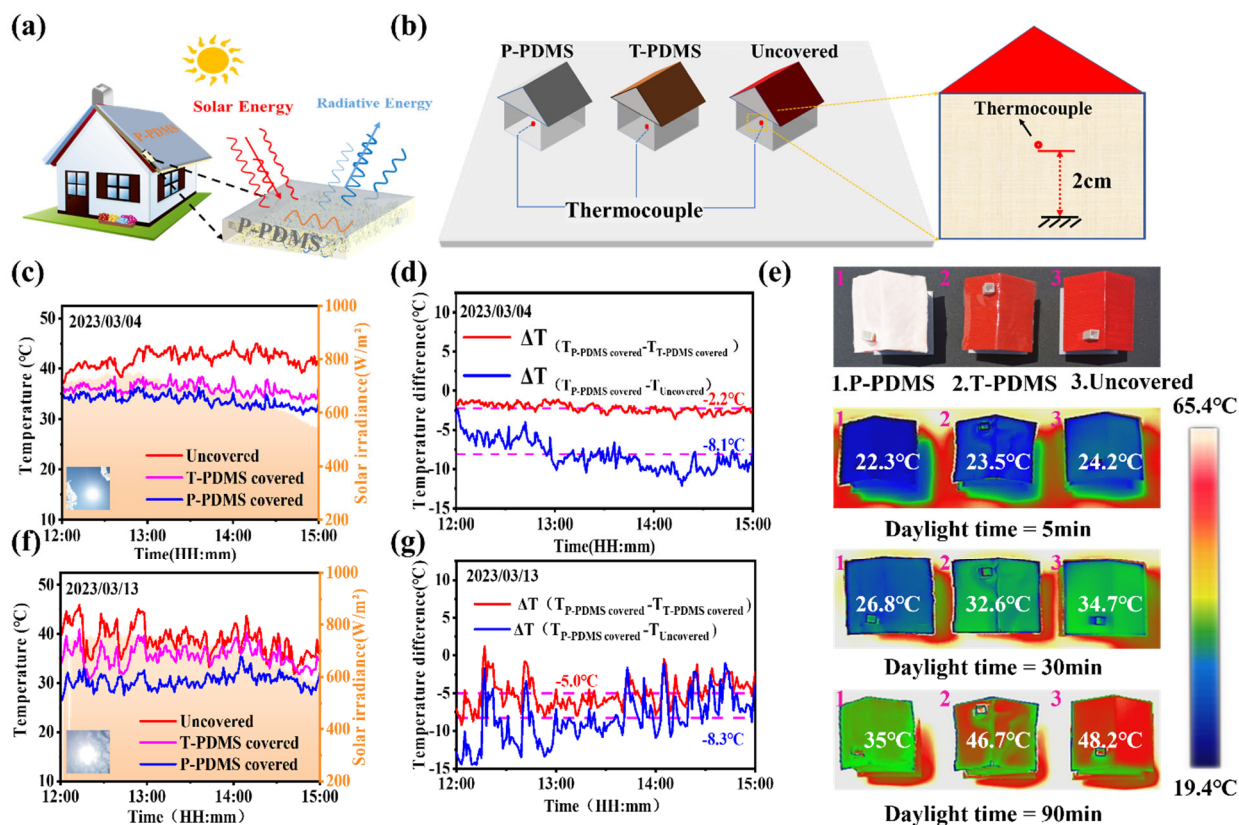
Refractive index  $n$  (Fig.3a) and extinction coefficient  $k$  (Fig.3b) were used to investigate the infrared emission performance of PDMS. As can be seen from the FTIR absorbance spectrum of P-PDMS in Fig 3c, the peak disappearance at 5.8 $\mu\text{m}$  indicates that CAM has been removed after 2h of immersion. Fig. 3d shows the optical reflectance of P-PDMS and T-PDMS films in UV–vis–NIR regions (0.2 ~ 2.5  $\mu\text{m}$ ). The average reflectance of the P-PDMS film is more than 75%, while the reflectance of the T-PDMS film is close to zero. The hierarchical porous structure of P-PDMS is employed to enhance the efficient reflectivity and scattering of solar radiation. The emissivity of P-PDMS and T-PDMS films in the mid-infrared (MIR) region (wavelength range of 2.5 ~ 25  $\mu\text{m}$ ) was plotted in Fig. 3e. The scattering performance of the porous cooler is higher when the characteristic size of the pore matches the electromagnetic wave length. P-PDMS has a higher emissivity in the MIR region than T-PDMS because most of the pore size of the porous sample is between 7.5 and 22.5  $\mu\text{m}$  (Fig S1). The hierarchical porous structure of the P-PDMS film is utilized to ensure strong solar spectral reflectivity and high MIR thermal emissivity, thus delivering good radiative cooling performance.



**Figure 3.** Optical properties of PDMS films. (a) Spectral refraction index  $n$  and (b) Extinction coefficient  $k$  of the T-PDMS material in the wavelength range of 0 ~ 20  $\mu\text{m}$  (The light blue shaded part is the atmospheric window with the range of 8 ~ 13  $\mu\text{m}$ ). (c) Fourier infrared spectra of CAM, P-PDMS (soaked in ethanol for 120 min), and PDMS were obtained within the wavelength range of 2 to 16  $\mu\text{m}$ . (d) Reflectance spectra of the P-PDMS and T-PDMS films under solar spectrum (orange shaded area) in the wavelength range of 0.2 ~ 2.5  $\mu\text{m}$ . (e) Spectral emissivity of the P-PDMS and T-PDMS films under MIR region (2.5 ~ 25  $\mu\text{m}$ ).

### 3.3 Application Test of the Outdoor

Through a series of model application comparison experiments, the excellent daytime outdoor cooling performance of P-PDMS membrane was further evaluated. There are 3 house models (7.5cm  $\times$  5cm  $\times$  5cm), two of which are covered with P-PDMS film and T-PDMS film, and the other model is a bare house without any film. Thermocouples are placed in the interior center of the house to measure temperature changes (Fig. 4b). The infrared images irradiated by different illumination times (5min, 30min, 90min) are shown in Fig 4e. As the irradiation time increases, the temperature of the roof slowly increases. After 90 min, the P-PDMS covered roof was 11.7 $^{\circ}\text{C}$  cooler than the T-PDMS covered roof and 13.2 $^{\circ}\text{C}$  cooler than the uncovered roof. The daytime temperature variations and solar intensity for the three house models from March 4 and March 13, 2023 are plotted in Figs. 4c and 4f. The corresponding temperature differences are shown in Figs. 4d and 4g. The results on March 13, 2022 show that under the condition of average solar irradiance of 626.74  $\text{W}/\text{m}^2$ , the indoor temperature of P-PDMS membrane room is 8.1 $^{\circ}\text{C}$  lower than the ambient temperature, and 5.0 $^{\circ}\text{C}$  lower than that of T-PDMS membrane room.



**Figure 4.** Applications of the P-PDMS film for cooling. (a) Schematic diagram of cooling performance of the house model with the P-PDMS film. (b) Schematic illustration of three identical house models (covered with P-PDMS film and T-PDMS film and exposed model). (e) Physical photographs and thermal imaging photographs of three identical house models (covered with P-PDMS film and T-PDMS film as well as exposed house models) are placed outdoors. (c, f) Temperature variation and solar intensity in the daytime from March 4th and 13th, 2023. (d, g) Temperature drops achieved by different samples matched with Fig.4d and Fig.4f.

## 4. CONCLUSIONS

In this study, the hierarchically flexible porous P-PDMS PDRC film was quickly fabricated by a simple sacrificial template method. The sponge structures of the film enhance light scattering and reflection. The average reflectivity of P-PDMS film in the visible range is higher than 75 %, and the average emissivity in the range of 8 ~ 13  $\mu\text{m}$  is 99.4 %. The film enabled an average sub-ambient temperature decrease up to 15.4°C, and the inside temperature of the P-PDMS covered house was 8.1°C lower than the sub-ambient temperature. Combined with efficient DRC capabilities and mass production compatibility, the P-PDMS provides a new strategy having a widely potential application in outdoor sustainable and energy-free daytime cooling characterization.

## DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## ACKNOWLEDGEMENTS

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