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HOW POLY (VINYLIDENE FLUORIDE-CO HEXAFLUOROPROPYLENE) (PVDF-HFP) SCATTERS SUNLIGHT: MECHANISMS AND APPLICATIONS IN PASSIVE RADIATIVE COOLING

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Keywords	***Abstract***
PVDF-HFP, passive radiative cooling, Mie scattering, porous polymers, solar reflectance, thermal emission, daytime cooling.	Passive radiative cooling (PRC) has emerged as a sustainable cooling technology capable of reducing surface temperatures without energy consumption by simultaneously reflecting incoming solar radiation and emitting thermal energy through the atmospheric transparency window (8–13 µm). Among the various materials investigated for passive daytime radiative cooling (PDRC), poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has attracted significant attention because of its high infrared emissivity, chemical stability, hydrophobicity, and ability to form hierarchical porous structures. The exceptional cooling performance of PVDF-HFP arises from its strong sunlight-scattering capability, which is primarily governed by Mie scattering from pores and embedded particles with dimensions comparable to solar wavelengths. This article reviews the fundamental mechanisms by which PVDF-HFP scatters

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	sunlight and discusses its applications in advanced radiative cooling systems. The relationship between pore morphology, refractive index contrast, scattering efficiency, and cooling performance is analyzed, together with recent advances in composite PVDF-HFP cooling films and nanofiber membranes.

1. Introduction

Passive radiative cooling (PRC) has emerged as an energy-efficient and environmentally sustainable technology for reducing surface temperatures without external power consumption. The concept relies on reflecting incoming solar radiation while simultaneously emitting thermal energy through the atmospheric transparency window (8–13 μm) into outer space. Among the various materials investigated for PRC applications, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has attracted significant attention because of its unique optical and structural properties.

PVDF-HFP is a fluoropolymer copolymer composed of vinylidene fluoride and hexafluoropropylene units. Its effectiveness in solar reflection is primarily attributed to its porous microstructure, which can be engineered through phase separation, electrospinning, or solvent-casting techniques. The presence of air-filled pores creates numerous interfaces with contrasting refractive indices, resulting in strong Mie scattering and multiple scattering events across the solar spectrum. Consequently, incident sunlight is efficiently reflected, minimizing solar heat absorption. In addition, the intrinsic molecular vibrations of PVDF-HFP provide high emissivity in the mid-infrared region, enabling effective thermal radiation to the cold sky.

These combined characteristics make PVDF-HFP a promising material for advanced passive radiative cooling systems, including building coatings, wearable cooling textiles, and energy-saving thermal management technologies.

2. Fundamentals of Passive Radiative Cooling

The net cooling power of a radiative cooling material depends on two optical requirements:

1. **High solar reflectance (0.3–2.5 μm)** to minimize solar heating.
2. **High infrared emissivity (8–13 μm)** to maximize thermal radiation into space.

The cooling power can be expressed as:

$$[\ P_{net} = P_{rad} - P_{solar} - P_{atm} - P_{non\text{-}rad}\ ]$$

where:

- (P_{rad}) = emitted thermal radiation,
- (P_{solar}) = absorbed solar energy,

- (P_{atm}) = atmospheric back radiation,
- ($P_{non\text{-}rad}$) = conductive and convective heat gain.

A material exhibiting high solar reflection and high infrared emission can achieve sub-ambient temperatures even under direct sunlight.

3. Optical Properties of PVDF-HFP

PVDF-HFP possesses several characteristics favorable for radiative cooling:

3.1 High Infrared Emissivity

The fluorinated molecular structure contains polar C–F bonds that exhibit strong vibrational absorption in the mid-infrared region. These molecular vibrations enhance thermal radiation within the atmospheric window, enabling efficient heat dissipation.

3.2 Porous Morphology

PVDF-HFP can be fabricated with interconnected micro- and nanopores through phase separation techniques. Such pores increase solar reflectance by introducing numerous air-polymer interfaces.

3.3 Chemical Stability

PVDF-HFP exhibits:

- Excellent UV resistance,
- Hydrophobic behavior,
- Mechanical durability,
- Weather stability.

These properties make it suitable for long-term outdoor cooling applications.

4. Mechanisms of Sunlight Scattering in PVDF-HFP

4.1 Refractive Index Contrast

The fundamental mechanism of solar reflection in porous PVDF-HFP is the refractive index mismatch between:

- PVDF-HFP ($n \approx 1.35–1.42$)
- Air-filled pores ($n \approx 1.0$)

When sunlight encounters these interfaces, scattering occurs due to abrupt changes in optical impedance. Strong scattering prevents light penetration and increases diffuse reflection.

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4.2 Mie Scattering

The dominant scattering mechanism is Mie scattering, which occurs when pore diameters are comparable to the wavelength of incident light.

For solar wavelengths: $\mathbf{0.3\ \mu m \leq \lambda \leq 2.5\ \mu m}$

maximum scattering occurs when: $\mathbf{d \approx \lambda}$

where (d) is pore diameter.

Studies show that micropores around 1.3 µm exhibit scattering efficiencies several orders of magnitude higher than very small nanopores, significantly enhancing solar reflectance.

4.3 Multiple Scattering Events

Hierarchical porous structures create repeated scattering events:

- Incident sunlight enters the porous network.
- Light is redirected multiple times.
- Probability of transmission decreases.
- Overall reflectance increases.

This multiple-scattering effect produces broadband reflection across visible and near-infrared wavelengths.

4.4 Hierarchical Pore Structures

Combining nano- and micropores broadens the scattering spectrum:

Pore Type	Scattered Wavelength Region
Nanopores	Visible light
Micropores	Near-infrared light
Hierarchical pores	Broadband solar spectrum

Hierarchical PVDF-HFP films have demonstrated solar reflectance values approaching 96%.

5. Enhancement Through Particle Incorporation

5.1 TiO_2 Particles

Titanium dioxide possesses:

- High refractive index,

- Strong visible and NIR scattering,
- Excellent weather resistance.

When incorporated into PVDF-HFP, TiO_2 particles increase solar reflectance through additional Mie scattering.

5.2 Al_2O_3 Particles

Aluminum oxide particles effectively scatter visible wavelengths and complement TiO_2 scattering in the near-infrared region. Bilayer PVDF-HFP/TiO_2–Al_2O_3 structures exhibit superior cooling performance because scattering functions are distributed across different layers.

5.3 SiO_2 Nanoparticles

Silica nanoparticles create additional scattering interfaces and improve infrared emissivity. PVDF-HFP/SiO_2 composite nanofibers have achieved solar reflectance close to 95% and emissivity above 97%.

6. Experimental Evidence of Scattering-Induced Cooling

Several studies have demonstrated the effectiveness of sunlight scattering in porous PVDF-HFP systems:

Material	Solar Reflectance	IR Emissivity	Cooling Performance
Porous PVDF-HFP film	96.4%	95%	~10.2°C below ambient
Hierarchical porous PVDF-HFP coating	~96%	~97%	~6 K sub-ambient
PVDF-HFP/TiO_2-Al_2O_3 bilayer membrane	90–95%	~98%	~12°C reduction
PVDF-HFP/SiO_2 nanofibers	94.9%	97.4%	~7.8°C daytime cooling

These results confirm that enhanced sunlight scattering directly contributes to improved cooling performance.

7. Applications of PVDF-HFP Radiative Cooling Materials

7.1 Building Envelopes

PVDF-HFP coatings can be applied to:

- Roofs,
- Exterior walls,
- Windows.

These coatings reduce indoor cooling loads and improve energy efficiency.

7.2 Wearable Cooling Textiles

Electrospun PVDF-HFP nanofibers are lightweight, breathable, and flexible, making them suitable for personal thermal management.

7.3 Vehicle Thermal Management

PVDF-HFP cooling films can lower surface temperatures in automobiles and outdoor equipment by reflecting sunlight and emitting thermal radiation.

7.4 Electronics Cooling

Passive cooling layers based on PVDF-HFP can reduce overheating in outdoor electronics and sensors without requiring external power.

8. Future Perspectives

Future research directions include:

- AI-assisted optimization of pore architectures,
- Multifunctional cooling and energy-harvesting systems,
- Self-cleaning and self-healing PVDF-HFP coatings,
- Large-scale manufacturing methods,
- Smart switchable radiative cooling materials.

Advanced control of pore size distribution and scattering interfaces will further enhance broadband solar reflection and cooling performance.

9. Conclusion

As heatwaves become more frequent and intense around the world, scientists are exploring new ways to keep buildings cool without increasing energy consumption. Researchers at the University of Sydney, working with startup Dewpoint Innovations, have developed a nano-engineered coating that reflects up to 97% of sunlight and stays significantly cooler than conventional surfaces. The experimental "smart paint" is designed to reduce heat absorption, lower indoor temperatures and potentially decrease reliance on air conditioning. It also has another unusual feature: the ability to capture moisture from the atmosphere and turn it into water droplets without using electricity. The breakthrough could offer a sustainable solution for urban areas struggling with rising temperatures, water scarcity and growing energy demands. PVDF-HFP is one of the most promising polymeric materials for passive daytime radiative cooling due to its combination of high infrared emissivity and exceptional sunlight-scattering capability. The primary scattering mechanism arises from Mie scattering generated by hierarchical porous structures and embedded particles. Air-polymer refractive index contrast, multiple scattering events, and broadband reflection collectively enable solar reflectance exceeding 95% in optimized systems. Recent advances involving TiO_2, Al_2O_3, and SiO_2 fillers have further improved cooling performance. As scalable fabrication methods continue to develop, PVDF-HFP-based cooling materials are expected to play an increasingly important role in sustainable building technologies, wearable cooling systems, and energy-efficient thermal management.

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