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Research Article

Assessing radiative cooling potential of polymeric films: A quality factor for energy-efficient materials

Vijayasimha Reddy Ireddy, Isabella Chiarotto, Daniele Ceneda, Alessandro Bile, Marco Centini, Maria Cristina Larciprete *

Dipartimento di Scienze di Base ed Applicate per l'Ingegneria, Sapienza Università di Roma, Rome, 00161, Italy

A B S T R A C T

We investigated the infrared radiation (IR) absorption coefficients of several polymer types to propose a novel approach through the development of radiative-cooling polymeric films and composites. We studied polymeric films and their infrared characterization for selective IR radiation absorption. Specifically, we prepared and analyzed films of Styrene-Isoprene-Styrene (SIS), Styrene-Butadiene-Styrene (SBS), and Styrene-Ethylene-Butadiene-Styrene (SEBS) copolymers for radiative cooling applications. The linear optical properties of the films in the mid-infrared range were characterized using Fourier-transform infrared (FT-IR) spectrophotometry.

To evaluate the cooling performance, we introduced a quality factor that accounts for emissivity within the two key infrared transmission windows of Earth's atmosphere. Based on the experimental results, we calculated the quality factor to compare the radiative cooling efficiency of the different investigated polymers.

1. Introduction

In the last years, environmental sustainability has emerged as the most challenging global issue. Among the different strategies, radiative cooling (RC) represents a promising approach to reduce global warming and to pursue clean energy. In detail, all bodies at any given temperature exchange heat with the universe, as it is the ultimate heat sink, through earth's atmosphere, allowing cooling without external energy. However, there are only two infrared atmospheric windows that allow emitted thermal infrared radiation to propagate without being absorbed by the water vapor and CO_2 dispersed into the atmosphere, namely 3–5 and 8–12 μm. Furthermore, all bodies absorb solar energy from the sun (~6000 K) and convert it into heat energy, so called photothermal effect.

In recent years, radiative cooling [1] has gained increasing attention for its potential to mitigate global warming by reducing energy consumption of buildings, and air conditioning systems of vehicles [2,3]. Polymeric materials, characterized by high emissivity values in the infrared range, and easiness of fabrication, are crucial in advancing radiative cooling technologies.

Automobile air conditioning systems use is identified as the largest contributor to the auxiliary energy consumption of cars (i.e. the part that is not used for propelling the vehicle), and hence has a great influence on fuel economy and associated emissions. In terms of energy saving numerous studies were carried out to improve the efficiencies in thermal transfers. Among those, radiative cooling has attracted tremendous interest because it enables materials to passively cool the surface without energy consumption [4].

As already mentioned, although the infrared radiation covers a very wide wavelength range, only a limited portion, which falls within the two transparency windows, is transmitted through the atmosphere [5]. The remaining IR radiation is mostly absorbed by water vapor and CO_2 dispersed in the atmosphere. In order to get efficient radiative cooling of a hot body, its surface should have high emissivity values in the transparency windows of the atmosphere which lies between 3–5 μm and 8–13 μm along with attenuated emissivity between 5 and 8 μm. As a consequence of such emissivity spectral behaviour, the infrared radiation which is thermally emitted from the surface to the surrounding space, can efficiently lead to surface cooling in a passive way. Additionally, minimizing absorption of incoming solar radiation in the visible and near-infrared (NIR) regions further enhances cooling efficiency.

Several structural geometries have been explored to improve selective wavelength absorption and infrared emissivity within the atmospheric window in both periodic and random systems [6]. In multilayer structures the refractive index contrast of component layers can be engineered to maximize emissivity or reflectivity in the 8–13 μm range [7]. Likewise, the influence of photonic structures on radiative cooling has been investigated by adjusting the dimensions of periodic nanostructure also in 2-D and 3-D configurations including gratings [8],

* Corresponding author.
E-mail address: mariacristina.larciprete@uniroma1.it (M.C. Larciprete).

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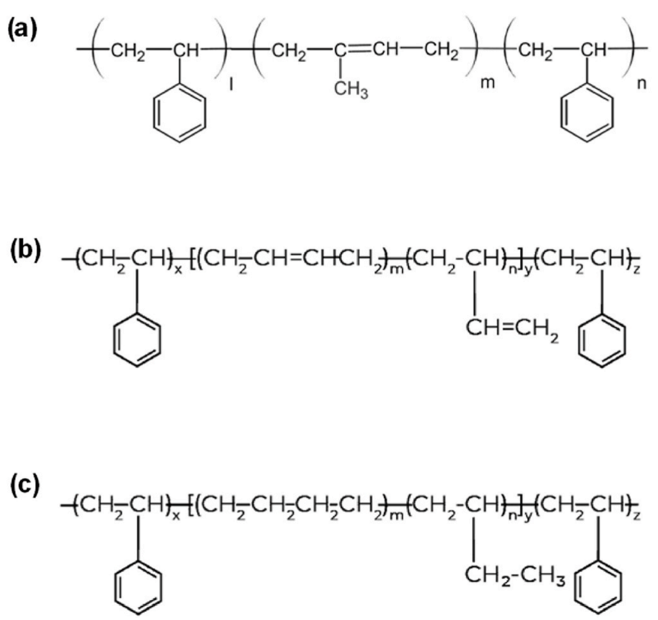

Fig. 1. (a) Styrene-Isoprene-Styrene (SIS); (b) Styrene-Butadiene-Styrene (SBS); (c) Styrene-Ethylene-Butadiene-Styrene (SEBS). Four different films composed by a) SIS, b) SBS, c) SBS extended with paraffinic oil (SBS oil) and d) SEBS extended with paraffinic oil (SEBS oil) were obtained from Versalis SPA. All the polymer materials were acquired in granular form.

periodic arrays of nanoresonators, nanopillars [9], nanopyramids [10] as well as in metal–dielectric–metal resonators [11], among others. Polymeric materials represent a compelling option for integration into photonic radiative cooling system offering versatility in two configurations. In random systems, they can act as the matrix of random radiative cooling devices, where nanopores or microscale inclusions scatterer incident solar light [12]. Additionally, polymers can play the role of the selective emitting layer atop reflective bottom layers, enhancing thermal emission properties.

Given this premise, in recent years, polymer-based radiative coolers have gained significant attention and been experimentally validated. This is primarily because transparent polymers exhibit low absorption in the solar spectral range, while offering high emissivity in the infrared (IR) region due to the characteristic IR fingerprint of organic molecules [13]. Furthermore, polymers offer the advantage of being easily manufactured on a large scale and at relatively low cost, making them a practical option for radiative cooling technologies.

In this work, we investigate a series of polymeric films prepared by drop casting followed by lift-off process. Optical characterization has been performed at room temperature in the mid-infrared range. Reflectance spectra, measured via FTIR highlight that the resulting films demonstrated promising radiative cooling performance as evaluated through the typical infrared transparency windows of IR radiation in the atmosphere. Finally, we employ detailed numerical modelling to evaluate the radiative cooling performance of the investigated films for both emissive and absorbance behaviour.

2. Material study

Thermoplastic elastomers (TPEs) represent important products in the polymer industry, with styrene-based block copolymers occupying the major portion of the TPE market. Styrene Block Copolymers are ideal for use in adhesive, sealant, and coating applications. These unique products have the physical properties of rubber, but the same system process of thermoplastics. Specifically, we investigated and compared the radiative cooling effectiveness of three styrene block copolymers (see Fig. 1), namely styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) and styrene-ethylene-butadiene-styrene (SEBS).

Table 1
Concentrations of starting polymeric solutions.

Material	Weight (mg)	Concentration (mg/ml)	Film Thickness (mm)
SIS	99,1	49,55	0,20
SBS	104,3	52,15	0,25
SBS (oil)	74,0	37,00	0,25
SEBS (oil)	87,0	43,50	0,30

a. Styrene-Isoprene-Styrene (SIS):

Styrene-isoprene-styrene or SIS block copolymers are popular primarily due to their combination of unique attributes [14]. This includes exceptional strength, lowest viscosity and lowest hardness among all SBCs, thus SIS is widely employed for easy thermoplastic processing.

b. Styrene-Butadiene-Styrene (SBS):

SBS block copolymers are used primarily for their compounding and adhesive qualities. It is widely used in asphalt pavements around the world for its excellent performance in high temperature resistance, low temperature cracking resistance, fatigue damage resistance, and water stability of asphalt mixtures [15].

c. Styrene-Ethylene-Butadiene-Styrene (SEBS)

SEBS is a multiblock copolymer that incorporates ethylene units along with styrene and butadiene, with particular attention to their radiative cooling properties [16]. SEBS, formed by hydrogenation of SBS copolymer, inherits SBS characteristics of SBS and is ozone resistant and chemical resistant (oil, detergents, acids, bases etc.). SEBS and SBS can also be used in modified applications with high oil ratio to provide good flexibility and excellent plastic modification effect.

3. Sample preparation

Toluene was employed as the solvent to create homogeneous solutions of varying polymer concentrations, as outlined in Table 1. The polymers were dissolved in toluene ($C_6H_5CH_3$) and maintained at 40 °C for 4 h under atmospheric conditions. In order to ensure the homogeneity of the solutions, they were stirred continuously for several hours. Afterwards, the polymer solutions were drop-cast onto glass test plates with a thickness of 0.2 mm and a diameter of 14 mm. The samples were then subjected to thermal treatment for 72 h to ensure the complete evaporation of any residual solvent.

4. Measurements

We characterized and compared the mid-infrared spectral features of several polymeric films in order to provide evidence of their different radiative cooling effectiveness.

FTIR spectroscopy (Fourier Transform Infrared spectroscopy) is a powerful analytical technique that offers significant advantages over traditional dispersive methods. These benefits include enhanced signal-to-noise ratio, the ability to obtain absorption spectra of low-energy, and the detection of weak absorption bands. This technique is extensively utilized for the study and characterization of resins and polymeric materials. It is also employed to evaluate the degradation of these materials under various service conditions and to analyse and diagnose defects that may occur during production or application processes.

Infrared reflection measurements were conducted using a Bruker Invenio-R FT-IR interferometer, covering the spectral range of 6000–400 cm^{-1}, or equivalently 1.6–25 μm. The IR source was a glowbar, while detection was performed using a deuterated triglycine

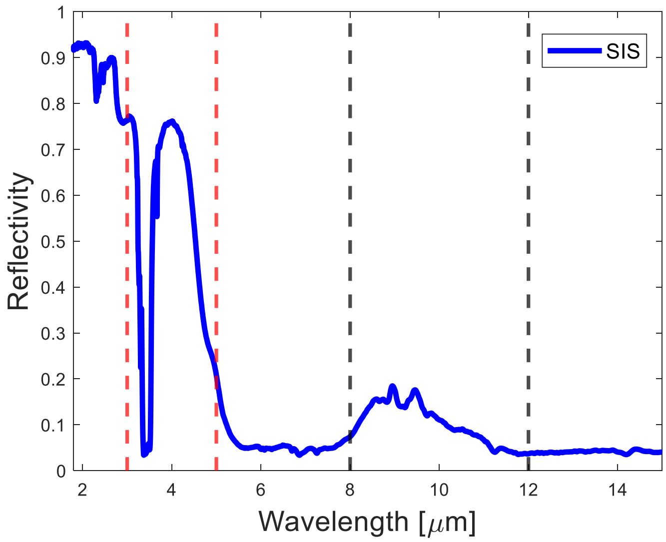

Fig. 2. FTIR spectral curve at 15° incidence angle and 0° polarization angle of a) SIS, b) SBS, c) SBS oil, d) SEBS oil.

sulfate (DTGS) pyroelectric detector. A total of 32 interferograms were acquired for each measurement, using a spectral resolution of 2 cm^{-1}. A sample area of 2.5 × 2.5 mm^2 was selected during IR data acquisition using windows apertures. The FT-IR platform is equipped with a reflectance unit allowing to set the angles of incidence and reflectance, from almost normal incidence (approximately 15°) to grazing angles (85°). The polarization state of incident light can be selected using a holographic polarizing filter with a motorized mounter. A set of measurements was conducted with an incidence angle of θ = 15°. All measurements were normalized using a gold reference mirror under identical experimental conditions, i.e. using the same polarization angle and incidence angle.

5. Results and discussions

For each measurement, reflectance spectra were recorded using two orthogonal linear polarization states of the incoming light. However, the experimental spectra obtained at near-normal incidence (15°) revealed no significant difference between light polarized perpendicular to the plane of incidence (s-polarization) and light polarized within the plane of incidence (p-polarization). Due to the lack of in-plane anisotropy, we present FT-IR spectra in reflection mode at a 15° incidence angle using s-polarized (0°) light for each sample.

We also evaluated the effect of the incidence angle by conducting measurements at a 45° incidence angle, however we found that the incidence angle did not significantly influence the measurements. As an example, the measured reflectivity for SIS sample is shown in Fig. 2 for θ = 15° incidence angle.

According to Kirchoff's law of heat radiation, the emissivity of a radiating body at a given temperature is equal to its absorptivity, under thermal equilibrium conditions, thus it can be retrieved as: A% = 1-R %-T%. The results, for all investigated samples, are displayed in Fig. 3 and summarize the absorbance spectral features from 650 to 4000 cm^{-1}. In order to focus on the atmospheric windows, we highlighted, with coloured bands, the two corresponding wavelength ranges on the graphs. As a first observation, the obtained experimental results display that there are considerable differences in the absorption of infrared radiation within the two atmospheric windows. In particular, SIS, SBS and SBS/oil films display higher absorption rate in the LWIR (i.e. 8-12 μm)

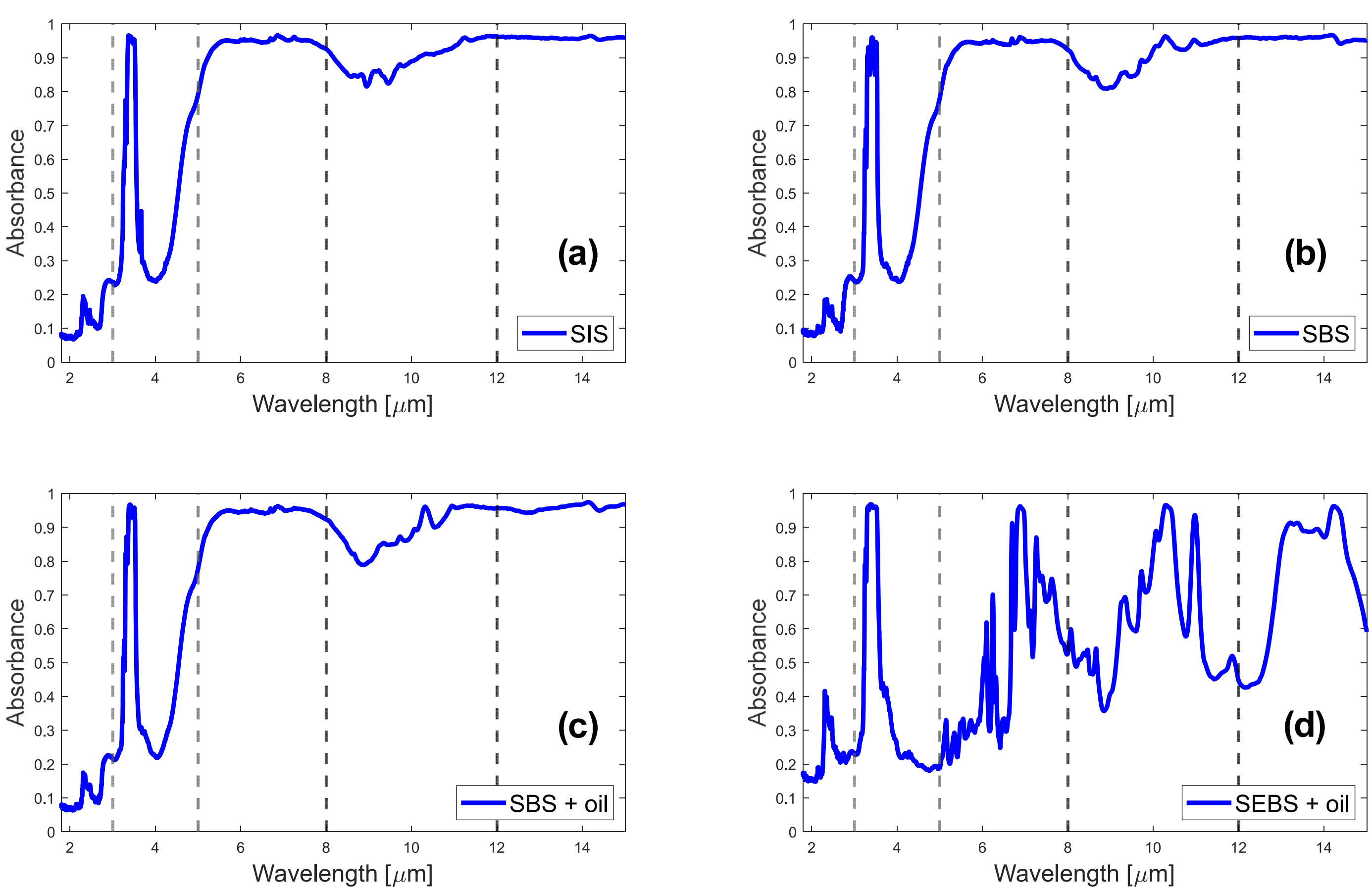

Fig. 3. FTIR spectral curve at 15° incidence angle and 0° polarization angle of a) SIS, b) SBS, c) SBS oil, d) SEBS oil.

Table 2
Different parameters described by Equations (1) and (2), calculated for 15° incidence angle and for light polarization stage 0° the samples SIS, SBS, SBS oil and SEBS oil.

	ϵ_{3-5}	ϵ_{8-12}	A_{MIR}	Q
SIS	0.53	0.89	0.17	8.35
	0.52	0.90	0.17	8.35
SBS				
	0.51	0.89	0.16	8.75
SBS + Oil				
	0.24	0.61	0.25	3.40
SEBS + Oil				

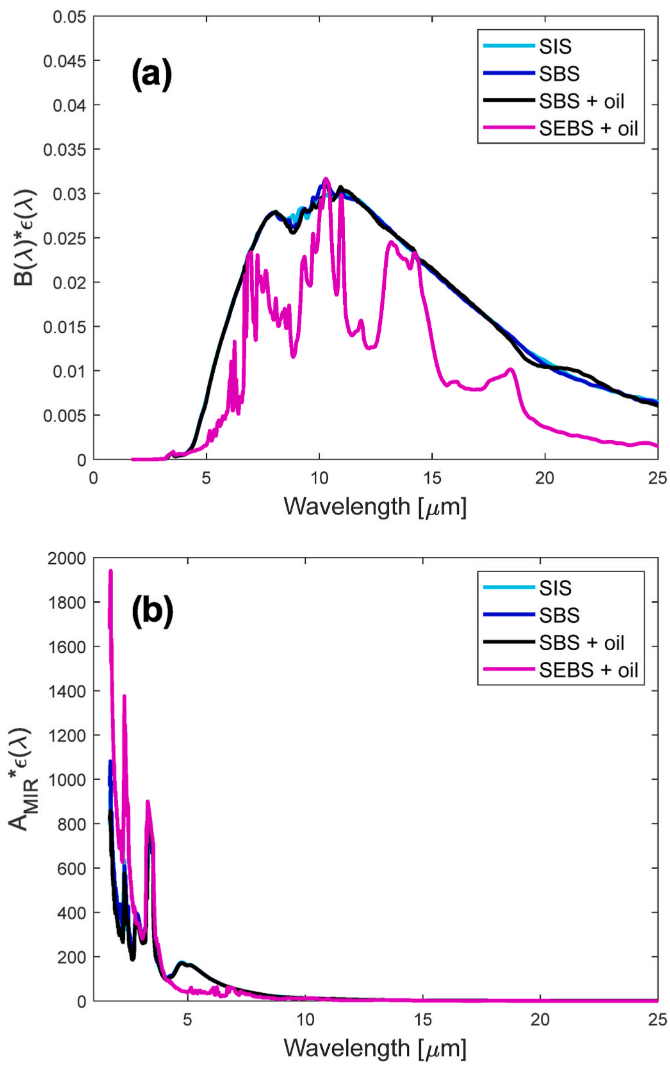

Fig. 4. Spectral emissivity for all investigated polymeric samples, calculated based on black-body emission at (a) 300K (room temperature) and (b) 6000K (Sun's surface temperature).

rather than in MWIR (i.e. 3-5 μm). On the other hand, SEBS/oil film exhibits comparable absorption rates in both MWIR and LWIR regions.

The spectra from SBS (Fig. 3b) and SBS/oil (Fig. 3c) films reveal no significant differences, indicating that the oil component does not have a dominant influence on the infrared absorbance of the films. Comparatively, SEBS exhibits lower absorbance values in the 5–8 μm range, along with reduced absorption in the long-wave infrared (LWIR) region.

In order to estimate and compare the radiative cooling efficiency of the samples, emissivity values can be evaluated across two distinct wavelength ranges: 3–5 μm and 8–12 μm, respectively [17].

For each wavelength range we thus calculated the average emissivity $\epsilon_{\lambda_{min}-\lambda_{max}}(\lambda)$ using the following formula:

$$\epsilon_{\lambda_{min}-\lambda_{max}}(\lambda) = \frac{\int_{\lambda_{min}}^{\lambda_{max}} B(\lambda)\,\epsilon(\lambda)\,d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} B(\lambda)\,d\lambda} \quad (1)$$

where $\epsilon(\lambda) = \alpha(\lambda) = 1 - r(\lambda)$ is the spectral emissivity at different wavelengths which can be retrieved from reflectance measurements. Similarly, $B(\lambda)$ is the black body radiation for a body at about 300 K (room temperature), $(\lambda, T) = \frac{2hc^2}{\lambda^5\left(e^{\frac{hc}{\lambda k_B T}}-1\right)}$, according to Planck's law with Planck's constant h and Boltzman k_B. These parameters hold for sample's emitted radiation within the two infrared atmospheric windows.

The behaviour at shorter wavelengths becomes important when considering that also the solar radiation contribute to infrared emissivity from the film. Although previous parameters were assessed to highlight films spectral emissivity properties, particular attention should also be given to $A_{MIR}(\lambda)$ i.e. the absorbance of infrared radiation emitted by the Sun within the whole MIR spectral range:

$$A_{MIR} = \frac{\int_1^{20} I_{solar}(\lambda)\,\alpha(\lambda)\,d\lambda}{\int_1^{20} I_{solar}(\lambda)\,d\lambda} \quad (2)$$

Here, $I_{solar}(\lambda)$ is the global solar intensity and is calculated using Planck's law for a body at 6000K (Sun's surface temperature).

The parameters described by Equations (1) and (2) both contribute to radiative cooling effectiveness during night and day behaviour, respectively, and are summarized in Table 2.

To obtain a quality factor that accounts for both emissivity and absorbance behaviour, we introduce the following function, where the average emissivity across the two atmospheric windows is normalized by the solar-radiation-weighted absorbance:

$$Q = \frac{\epsilon_{3-5}(\lambda) + \epsilon_{8-12}(\lambda)}{A_{MIR}} \quad (3)$$

The Q values, calculated for all the investigated polymers, are also reported in Table 2.

Notably, the SEBS + oil film shows a lower average emissivity, calculated based on black-body emission at room temperature, compared to other polymers, as seen in Fig. 4a. However, when considering infrared radiation from the Sun, the lower wavelengths become more influential, as illustrated in Fig. 4b, leading to an increase in the A_{MIR} factor at these shorter wavelengths. Ideally, this analysis would extend into the visible range, but our experimental setup is limited to wavelengths above 1 μm. Additionally, since the samples exhibit high transmissivity in the visible range, we assume that absorbance in this region remains neglectable.

Finally, it's worth to mention that the chain length and molar mass distribution are responsible of the material's vibrational modes that contribute to IR absorption. The investigated samples are styrene block copolymers with a molecular chain of the form styrene-*M*-styrene where M is Isoprene, Butadiene and (Ethylene-Butadiene), respectively. Consequently, the chain lengths are quite different, depending on the M-block. However, beside the nominal length of the blocks, to connect chain length to IR properties, further combined studies, as size exclusion chromatography for instance, would be necessary to assess the chain length and to determine the molecular weight distribution of a polymer.

6. Conclusions

In conclusion, we explored the infrared (IR) absorption properties of various polymer types to propose a novel approach for developing radiative-cooling polymeric films and composites. Our study focused on the preparation and infrared characterization of polymeric films tailored for selective IR absorption targeting radiative cooling applications. The linear optical properties of these films in the mid-infrared region were experimentally investigated using Fourier-transform infrared (FT-IR) spectrophotometry, providing critical insights into their potential for enhancing radiative cooling efficiency. To gain insights into the experimental findings, we developed a numerical model to assess the radiative cooling performance of polymeric films, considering both emissive and absorbance behaviours. This model yields an optimized parameter for low emissivity within atmospheric windows as well as reduced solar radiation absorption. This approach offers a promising method for evaluating the radiative cooling properties of various polymers, facilitating the selection of materials with significant potential for energy-efficient building design and climate control strategies.

CRediT authorship contribution statement

Vijayasimha Reddy Ireddy: Investigation. **Isabella Chiarotto:** Resources, Methodology, Conceptualization. **Daniele Ceneda:** Methodology, Investigation. **Alessandro Bile:** Investigation. **Marco Centini:** Methodology, Investigation, Conceptualization. **Maria Cristina Larciprete:** Supervision, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Maria Cristina Larciprete reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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