Silica Sphere embedded in TPX matrix for Radiative Sky Cooling

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ME 461 Engineering Material
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Introduction & Problem Statement

Most methods of cooling an object on Earth necessitate active cooling systems that require the use of energy. Traditional cooling systems make up 17% of the world's energy demands [1]. Much of this energy is generated using fossil fuels, which in turn lead to rising global temperatures. Furthermore, many common refrigerants are toxic to humans or harmful to the environment. Radiative sky cooling presents an alternative to these harmful, power hungry methods. Radiative cooling materials emit and reflect more heat than they absorb, allowing for passive cooling. Ideally, the material should be a perfect reflector in the solar spectrum (0.5-2.5 μm) and have a thermal emission peak that aligns with the atmospheric transparency window (8–13 μm) in the infrared. This allows the thermal radiation emitted from the surface to escape into space, thus cooling the body. Such cooling effect becomes increasingly important due the energy demand and overall increased heating, especially in urban areas. Increased energy consumption is seen to raise overall ambient temperature, leading to a cyclical reliance.

Recent developments allow these materials to cool objects even in direct sunlight. Even within this category of materials, there are a wide variety of options. The earliest designs made use of a multilayer structure, with several emissive materials placed in layers atop a layer of silver, chosen for its high reflectivity of solar radiation [1]. As material processing techniques advanced, nanofabricated metamaterials were also developed. These materials incorporate specifically designed microscopic structures to achieve passive daytime cooling. Both of these techniques are expensive and difficult to scale. As such, they are not suited for widespread adoption. A cheaper method of producing sky cooling materials is randomly distributing inorganic particulates in a polymer matrix. Recent developments in silica-based coatings and nanoparticle-doped polymers have demonstrated effective radiative cooling powers, providing significant cooling under direct sunlight. One of the most promising materials for daytime radiative cooling is silica, particularly in the form of microspheres embedded within polymethylpentene.

Material Properties

Silica microspheres with a silver lining will be added to the hybrid film to achieve radiative cooling. While TPX, silver, and silica work together as a system, their individual properties contribute to achieving the desired goal. Silica, which belongs to the ceramic family, provides strong scattering and emission properties. TPX, classified as a polymer, complements the assembly with its lightweight and flexible characteristics and acts as a binder for the silica microspheres.

Silica microsphere size can range from 5 to 100 µm. The microspheres are made of amorphous silica, a lack of crystalline structure. They exhibit high crush strength, making them suitable for applications involving high-shear forces and high pressures like plastic compounding and injection molding. Advances in hollow glass microsphere technology, such as 3M's iM30K product [15], have achieved compressive strengths of 30,000 psi (~200 MPa) at a density of 0.6 g/ml, offering a strong strength-to-density ratio. Glass microspheres also have superior thermal properties due to their high melting point, typically ranging from 500°C to 800°C [13].

Silica allows most visible light to pass through because it has low absorption in the visible spectrum. This property is attributed to its low refractive index which is a measure of how much light bends when passing through a material. However, silica glass is opaque for wavelengths shorter than 200 nm and longer than 3.5–4.0 µm. The key absorption bands occur in specific regions below 160 nm due to electron interactions, impurities, and OH groups. Between 2.73–4.3 µm are caused by OH groups and finally between 9–23 µm due to Silica vibrational resonances. Notably, silica exhibits strong absorption in the infrared range, particularly at 8 µm and 20 µm, where these vibrational resonances enable it to emit thermal radiation efficiently. The vibrational resonances of the Si–O bonds in silica are where the bonds naturally oscillate and interact with infrared radiation. These properties make silica ideal for applications such as radiative cooling, as it allows visible light to pass through while strongly emitting heat through specific infrared wavelengths [16].

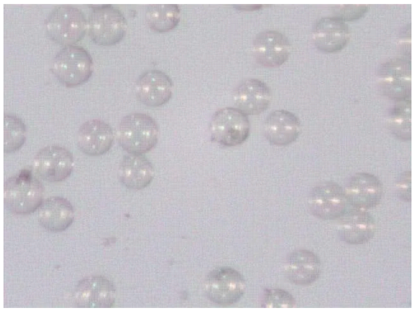

Figure 1: Hollow glass Silica Microspheres. Retrieved from Microspheres Online [14]

Silica exhibits strong scattering in the solar spectrum because of the high refractive index contrast between silica and air. High refractive index contrast between silica and air means that the refractive index which of silica is significantly different from that of air. This difference in refractive index causes light to scatter or reflect strongly when it interacts with silica particles or fibers. The scattering efficiency is highly dependent on the particle size of silica, with optimal performance achieved when the particle size is comparable to the wavelength of the incident light. For silica spheres, this results in a resonant scattering effect, where light is effectively reflected rather than transmitted through the material. The optimal radius for silica particles varies depending on the target wavelength, but it typically ranges between 75–275 nm for the visible and near-infrared spectrum.

The coating of silver added another layer of reflectivity to the layers. Silver is one of the most reflective metals scoring a reflectivity of 97% [5]. Silver reflects a significant portion of incoming solar radiation, preventing the absorption of solar energy by the material. Without a reflective substrate like silver, some of the emitted thermal radiation from the hybrid film could be absorbed by the underlying surface, significantly reducing the overall cooling efficiency**.**

The TPX matrix used in the film serves the purpose of introducing plasticity into the hybrid material. TPX, a thermoplastic polymer, exhibits relatively low density, low surface tension and heat resistance [2]. Such characteristics of the material are ideal for creating films due to lower costs and lightweight structure. While other polymers such as polyethylene may display visible transparency, important for the effectiveness of the film, they display some solar absorption [3].

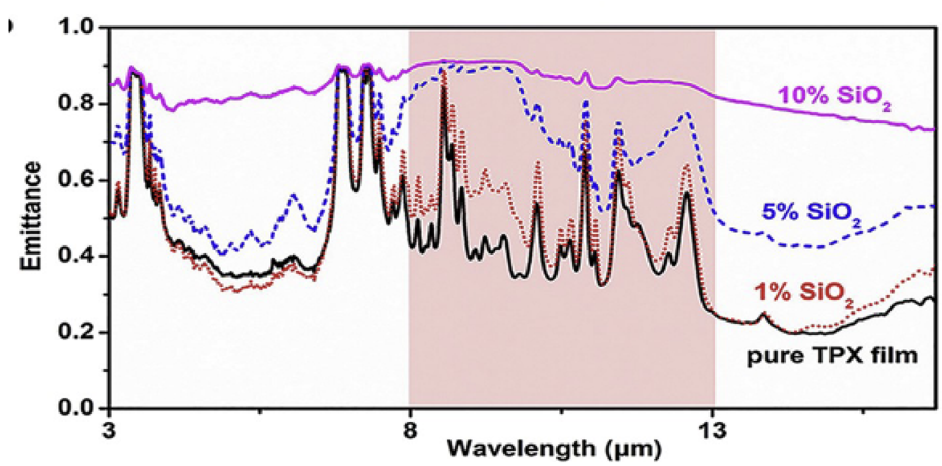

Figure 2: Emittance of silica-TPX hybrid film with a constant thickness but varying silica concentration. Red portion highlights the thermal infrared radiation wavelengths of concern for emittance to outer space. Reprinted from *Nanoporous silica microspheres–polymethylpentene (TPX) hybrid films toward effective daytime radiative cooling* by Yang J. et al 2020.

When the two metamaterials are combined, the processing of the material becomes important to the optical behavior that is desired. Emissivity for reflection is dependent on the thickness of the composite coat applied and the absorption the material is capable of, i.e. large thickness and absorption capability leads to high emissivity, though the increase of the silica quantity is able to improve upon the scattering effects of the material. However, another metric to impose upon when it comes to a higher concentration of silica sphere is emittance in other wavelengths. A 10% concentration of silica to TPX displayed the highest emittance in the thermal infrared radiation wavelength but a 5% ratio is deemed more ideal due to the lower emittance in other bands (figure 2). The increase in the scattering of visible lights improves the reflectance and cooling properties of the film. However, it is important to note that a balance of the added silica spheres is needed to limit the emittance into wavelengths outside of the atmospheric transparency window (8-13 μm)[3]. It is important for both of the metamaterials to experience little to no absorption and not heat up when exposed to solar irradiation.

Microstructure

The cooling abilities of this material arise from the combination of the three components: a silver layer, TPX substrate, and silica microspheres. The high reflectivity of the silver coating is due to the atomic structure of silver. Like copper and gold, two other group 11 elements, silver has only one valence electron. More valence electrons would impede electron motion, reducing reflectivity. The ductility of silver makes it suitable for thin coatings. Silver has a face-centered cubic structure, with a higher number of slip planes and slip directions than other crystal structures allowing for greater plastic deformation. Finally, as a noble metal, silver has a full d-subshell. This reduces the reactivity of silver, preventing many impurities from forming, further contributing to its ductility.

TPX, or polymethylpentene, is a linear polymer. The weak Van der Waals interactions between the linear chains give TPX flexibility, allowing it to be used as a thin film. The stereochemistry is isotactic. This leads to a semicrystalline structure, increasing the strength of the polymer and making TPX opaque in bulk quantities. However, thin films are transparent, as is required by this application. It is also composed entirely of hydrogen and carbon, giving it a relatively low density.

The emissivity of silica microspheres is due to the interaction between charged particles with the silica structure. First, some background. Within solid bodies, the motion of any individual particle is subject to innumerable forces. The electromagnetic force from any other charged particle, which may itself be moving, can affect the motion of a particle. All of this makes it impossible to accurately model the motion of a charged particle through a solid. This can present an issue, as the acceleration of charged particles is what causes the emission of the radiation required for radiative cooling. Introducing a conceptual model for groups of particles and the excitations that travel through them greatly simplifies any description of motion. Such a model is referred to as a quasiparticle [4]. Two quasiparticles are of interest herein: phonons and polaritons. Phonons are a representation of excitations in the structure of a material, specifically silica in this case. These excitations, much like photons, are quantized. Phonons can take the form of electric or magnetic dipoles. When these dipoles interact with photons, they form a new resonating quasiparticle called a phonon-polariton. These resonating dipoles have high emissivity, but the optimal size of these spheres must be determined. Zhai et al. (2017) compared the normalized absorption, scattering, and extinction to the size parameter (k_0a) of these spheres. The size parameter is a dimensionless quantity equal to the angular wave number (k_0) multiplied by the radius of the sphere (a). The results can be seen in Figure 3. The extinction, shown in black, is the sum of the absorption and scattering. This value peaks around 2.5, equivalent to a diameter of 4µm for a wavelength of 10µm, roughly the middle of the atmospheric window.. This shows, experimentally, that using silica microspheres of this size will have the best emissivity in the atmospheric window.

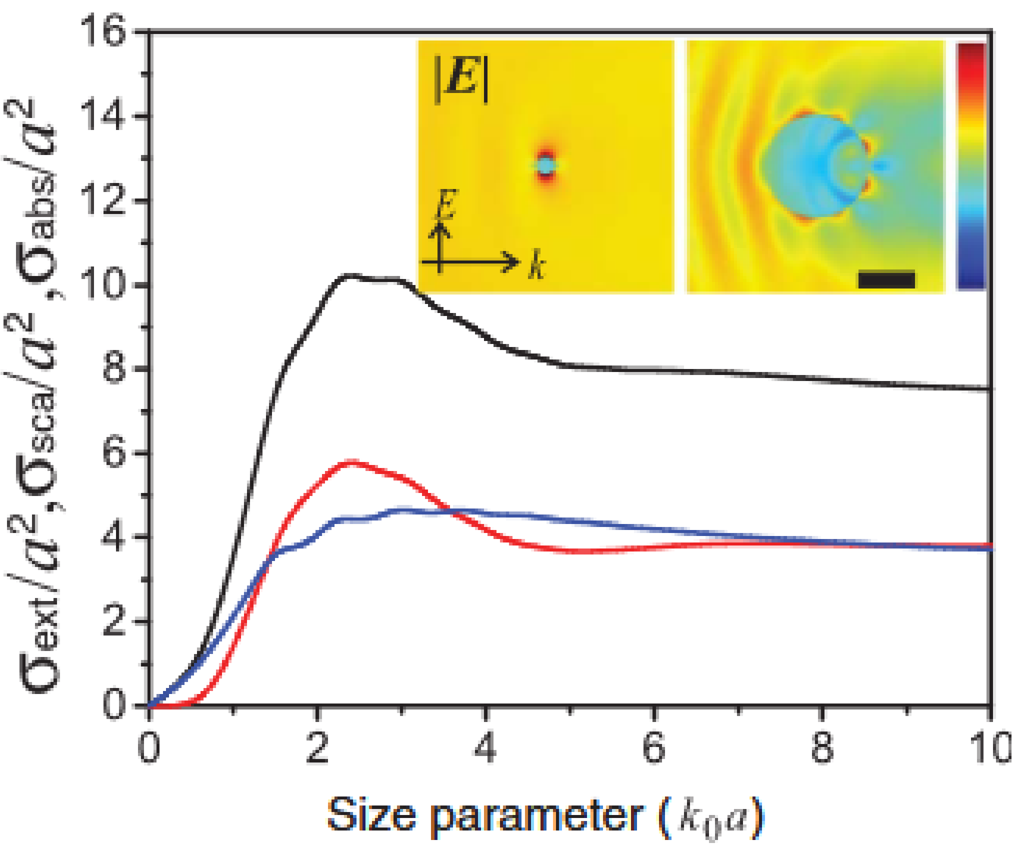

Figure 3: Normalized absorption (blue), scattering (red), and extinction (black) vs size parameter. The illustration in the top right shows the electric field distribution around two spheres with 1- and 8-µm diameters. Scale bar of 4 µm. Reprinted from *Scalable-manufactured randomized glass-polymer hybrid metamaterial for daytime radiative cooling* by Zhai et al, 2017

Processing

Several fabrication methods have been proposed in the embedding of silica spheres within polymer matrices. In an approach by [3], roll to roll printing (R2R) was used in fabricating such materials. An alternative method proposed by [4] involves the deposition of SiO2 microsphere-TPX hybrid films on fluorine-doped tin oxide (FTO) substrates using the tape casting technique. Polymer matrices are used primarily for its lightweight and ease to work with during applications. Polymers are often used as a plasticizer for the compounding material and enhance mechanical properties such as toughness.

Polymer matrices (TPX) can easily be manufactured into a meta material with varying sized silica microspheres. In [3], such hybrid material was able to be produced at a rate of 5 m/min through a R2R manufacturing process. The fabrication begins with the creation of a mold featuring trench-like polymer metasurfaces. This mold is produced using a high-precision laser 3D nanoprinting system, to achieve a low surface roughness on the nanoscale. Minimal surface defects are ideal to optimize the optical properties of the finished product (specifically less than the wavelengths of the atmospheric transparency window). Using the R2R photo-imprinting process, the mold transfers its designed structures to the polymer film. During this step, the silica microspheres are embedded into the TPX matrix. These microspheres are the ones providing the functionality of scattering and emitting thermal radiation [7]. Silica spheres deposition amounts can be controlled by the use of a gravimetric feeder. Relatively uniform concentration can be observed. Deposition of FTO substrates is done after the imprinting of the polymer (figure 4). Varying the depth of imprinting indentation is seen to increase surface area and lead to larger cooling matrices.

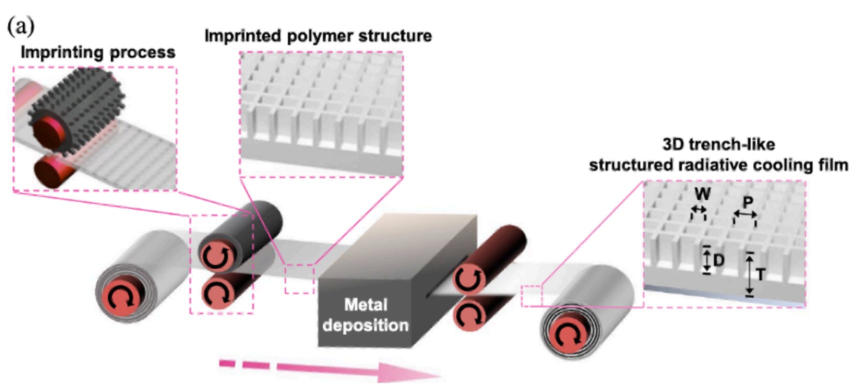

Figure 4:Roll-to-Roll imprinting process starting from molded indenters created from high precision laser 3D nanoprinting systems to metal depositions into trench structure of the silver substrates. Reprinted from *Highly efficient flexible structured metasurface by roll-to-roll printing for diurnal radiative cooling* by Lin, K.T. et al, 2023.

Tape casting [8] is a wet shaping ceramic processing method, composed of a solvent, polymer binder, and ceramic particles. In the method done in [4] solid SiO2 microspheres are replaced with nanoporous microspheres of the same regular spherical shape to improve the physical contact between the microspheres and the TPX polymer matrix. Additionally, SiO2 particles of two different mean sizes (4.5 µm and 6.5 µm) are incorporated as inert fillers to minimize shrinkage and enhance the mechanical stability of the composite. The silica spheres are left to dry while the TPX dissolves in the solvent. Once the process is complete, the two materials are then joined together. In application, the solution is deposited on the FTO substrate via tape casting for several hours before the final metamaterial is created.

Optimizing the composite material during tape casting, uniformity and well distribution of the silica sphere is an important factor when it comes to the finish of the final product. Due to this reason, introduction of ultrasonic irradiation using an ultrasonic probe can decrease the likelihood of large defects commonly present in ceramic materials. Fast evaporation rate of the organic liquid during the deposition process of the silica can lead to crack formation. Controlling the evaporation rate of the liquid from the mixture gives the polymer more chances to precipitate from the solvent, ultimately leading to a more uniform structure formation (figure 5).

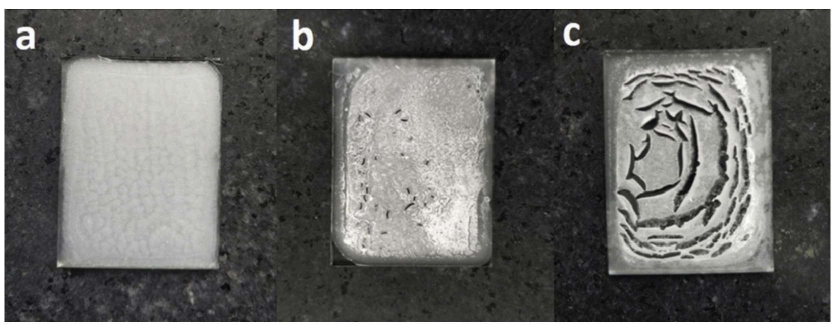

Figure 5: Preparation of silica-TPX through tape casting in different conditions: (a) ultrasonic irradiation with sealing (b) without ultrasonic irradiation (b) without ultrasonic irradiation nor sealing. Reprinted from *Nanoporous silica microspheres–polymethylpentene (TPX) hybrid films toward effective daytime radiative cooling* by Yang J. et al, 2020.

Applications

The advancements in radiative cooling materials have opened opportunities for varying application in energy conservation, sustainable infrastructure, and environmental protection. The passive cooling properties of SiO2-TPX hybrid materials, along with their versatility and cost-effectiveness, make them suitable for practical use. For instance, these materials can be applied to rooftops and building facades to passively lower indoor temperatures by reducing heat absorption and increasing thermal emission. This decreases reliance on air conditioning systems, leading to decreased energy consumption and greenhouse gas emissions [3], [9]. Similarly, their use on vehicle surfaces can mitigate overheating under direct sunlight, improving passenger comfort and reducing the energy demand for air-conditioning. Thermal imaging tests have demonstrated cooling effects on car hoods when coated with these films [7].

Radiative cooling materials also play an important role in solar energy applications. By lowering the operational temperatures of solar cells, the materials minimize any efficiency losses caused by overheating. The material's ability to reflect solar irradiance while emitting infrared radiation helps maintain optimal performance [10], [11]. Additionally, thermal power plants can benefit from these materials by integrating them into cooling systems to improve efficiency. Their passive nature reduces water consumption for cooling, which addresses environmental concerns regarding water scarcity.

Adoption of radiative cooling materials on a large-scale also results in significant environmental benefits. By replacing traditional cooling systems, these materials reduce dependency on fossil fuels and limit the release of harmful refrigerants into the atmosphere [1], [9]. The lightweight and scalable properties of SiO2-TPX hybrid materials make them suitable for portable devices as well, where effective heat management is crucial for things like electronics and portable cooling systems [6], [12].

The benefits of these materials include energy efficiency, versatility, and sustainability. Their high solar reflectance and strong emissivity allow for significant reductions in cooling-related energy use [12], [9] . Manufacturing techniques such as roll-to-roll printing and tape casting ensures cost-effective production which makes widespread adoption possible [12], [7].

Conclusion

Silica-TPX is an ideal candidate for the purpose of radiative sky cooling due to the individual optical and mechanical properties which are enhanced through embedding in the silica into a TPX matrix. Due to the limited solar absorption of the two materials, absorption rate is relatively low. Based upon the current research done in optimizing the processing of the material, concentration of the silica spheres in the material can determine the emittance in the atmospheric transparency window. Attention to the processing in providing a uniform material limits the amount of defects interfering with the final optical properties. Due to the small-scale nature of working in the infrared radiation wavelength, high precision must be achieved, which can be done with the use of laser printing in R2R printing or by use of ultrasonic irradiation during tape casting. Optimizing these properties for the material is ultimately meant to be used for energy conservation and incorporated into sustainable design for cooling. Due to the passive nature of the radiative sky cooling method, the material is flexible in the possible application in need of cooling.

References

[1]Yu, X., Chan, J., & Chen, C. (2021). Review of radiative cooling materials: Performance evaluation and design approaches. *Nano Energy, 88* (106259). https://doi.org/10.1016/j.nanoen.2021.106259

[2] *Westlake Plastics TPX® Polymethylpentene*. MatWeb. https://www.matweb.com/search/datasheet.aspx?matguid=ab2e7979b9e74c0e862cc48d3f760188.

[3] Zhai, Y., Ma, Y., David, S. N., Zhao, D., Lou, R., Tan, G., Yang, R., Yin, X. (2017). Scalable-manufactured randomized glass-polymer hybrid metamaterial for daytime radiative cooling. *Science.* DOI: 10.1126/science.aai789.

[4] Universität Münster (n.d.) *What are Quasi Particles? https://www.uni-muenster.de/Physik.AP/Demokritov/en/Forschen/Forschungsschwerpunkte/mBECwaqp.html*

[5] Wu, H.-Y., Huang, S.-R., Shih, C.-H., Hsiao, L.-J., Chen, H.-W., Cheng, M.-C., & Hsu, J.-C. (2022). Highly reflective silver-enhanced coating with high adhesion and sulfurization resistance for telescopes. *Nanomaterials*, *12*(7), 1054. https://doi.org/10.3390/nano12071054

[6] Yang, J., Gao, X., Wu, Y., Zhang, T., Zeng, H., & Li, X. (2020). Nanoporous silica microspheres–polymethylpentene (TPX) hybrid films toward effective daytime radiative cooling. *Solar Energy Materials and Solar Cells*, *206*, 110301. https://doi.org/10.1016/j.solmat.2019.110301.

[7] Lin, K.-T., Nian, X., Li, K., Han, J., Zheng, N., Lu, X., Guo, C., Lin, H., & Jia, B. (2023). Highly efficient flexible structured metasurface by roll-to-roll printing for diurnal radiative cooling. *eLight*, *3*(1). https://doi.org/10.1186/s43593-023-00053-3.

[8] Nishihora, R. K., Quadri, M. G., Hotza, D., Rezwan, K., & Wilhelm, M. (2018a). Tape casting of polysiloxane-derived ceramic with controlled porosity and surface properties. *Journal of the European Ceramic Society*, *38*(15), 4899–4905. https://doi.org/10.1016/j.jeurceramsoc.2018.07.016.

[9] Zhao, D., Aili, A., Zhai, Y., Xu, S., Tan, G., Yin, X., & Yang, R. (2019). Radiative sky cooling: Fundamental principles, materials, and applications. *Applied Physics Reviews*, *6*(2). https://doi.org/10.1063/1.5087281

[10] Zhu, L., Raman, A. P., & Fan, S. (2015). Radiative cooling of solar absorbers using a visibly transparent photonic crystal thermal blackbody. *Proceedings of the National Academy of Sciences*, *112*(40), 12282–12287. https://doi.org/10.1073/pnas.1509453112

[11] Hao, J., Lheurette, É., Burgnies, L., Okada, É., & Lippens, D. (2014). Bandwidth enhancement in disordered metamaterial absorbers. *Applied Physics Letters*, *105*(8). https://doi.org/10.1063/1.4894181

[12] Feng, J., Santamouris, M. and Gao, K. (2020) ‘The radiative cooling efficiency of silica sphere embedded polymethylpentene (TPX) systems’, *Solar Energy Materials and Solar Cells*, 215, p. 110671. https://doi.org/10.1016/j.solmat.2020.110671

[13] AZoM. (2024). *Silica - silicon dioxide (sio2)*. https://www.azom.com/article.aspx?ArticleID=1114
[14] Microspheres Online (n.d.). *Properties of Microspheres.* https://microspheres.us/properties-of-microspheres/.
[15] *3MTM Glass Bubbles iM30K*. 3M in the United States. 3MTM. https://www.3m.com/3M/en_US/p/d/b40064617/
[16] Lo Piccolo, G. M., Morana, A., Alessi, A., Boukenter, A., Girard, S., Ouerdane, Y., Gelardi, F. M., Agnello, S., & Cannas, M. (2021). Ultraviolet-visible light-induced solarisation in silica-based optical fibres for indoor solar applications. *Journal of Non-Crystalline Solids*, *552*, 120458. https://doi.org/10.1016/j.jnoncrysol.2020.120458