

Incorporation of solar reflective nanomaterials in High-Pressure Laminates for exterior façades

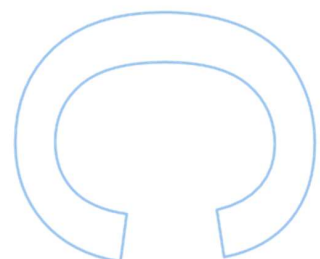
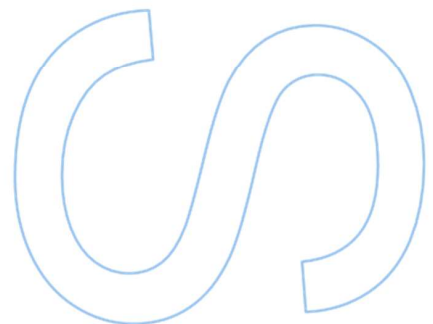
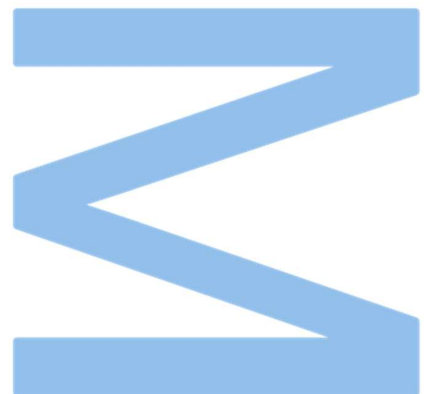
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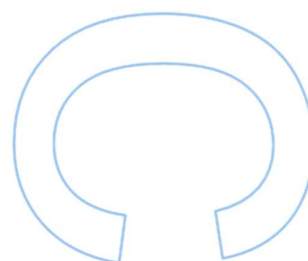
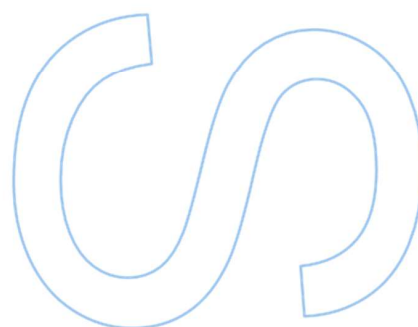
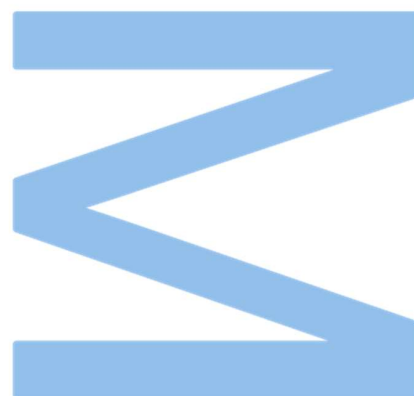
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UNIVERSIDADE DO PORTO

Abstract

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

MSc. Engineering Physics

Incorporation of solar reflective nanomaterials in High-Pressure Laminates for exterior façades

by [Alexandra SANTOS](#)

Under the background of global warming and rising temperatures, there is a considerable worldwide energy demand for cooling systems. Moving towards energy-efficient buildings, passive temperature regulation, not requiring any power input and with no greenhouse gas emissions, is an appealing alternative to mitigate the cooling demands in buildings. Near-infrared radiation (NIR) comprises about 50% of the total solar energy reaching Earth, and incorporating NIR reflective materials, with visible light transparency to avoid visual alterations, in high-pressure laminates (HPLs) for exterior façades is a promising approach to diminish the temperatures reached. In this work, the effect of incorporating NIR reflective materials, namely SiO_2 1 μm and 60-70 nm and TiO_2 50 nm, on HPL was evaluated for the improvement of the optical and thermal performance in order to reduce the cooling needs. Embedding NIR reflective materials on the overlay and decorative paper of an HPL leads to an improvement of the reflectance compared to a standard HPL, with satisfactory colour alterations. The production of HPL with an exterior grade (EG) film was carried out with decorative paper doped with SiO_2 nanoparticles since they led to the highest reflectance improvement. Despite the 7.5 wt% sample exhibiting the highest NIR and total reflectance enhancement relative to a standard HPL ($\Delta R_{\text{NIR}} = 37.4\%$ and $\Delta R_{\text{Total}} = 31.6\%$), the colour alterations obtained were above the threshold of $\Delta E = 3$. Thus, the 5 wt% SiO_2 -doped EG HPL was selected as the optimal sample, considering the relative reflectance increase ($\Delta R_{\text{NIR}} = 31.6\%$ and $\Delta R_{\text{Total}} = 23.5\%$) and colour-alterations, which were satisfactory ($\Delta E = 1.5$). To improve the distribution of particles, SiO_2 nanoparticles were dispersed in PMMA resulting in a

greater enhancement of reflectance ($\Delta R_{NIR} = 23.5\%$ and $\Delta R_{Total} = 22.9\%$) compared to a dispersion in water, with acceptable colour changes ($\Delta E = 1.5$) compared to the standard. The FTIR spectrum of the doped HPLs exhibited significant absorbance/emittance in the atmospheric transparency window (ATW), indicating a potential to release excess heat. This study allowed us to reach favourable results regarding the incorporation of NIR reflective materials on HPLs, opening the door for additional applications.

UNIVERSIDADE DO PORTO

Resumo

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

Mestrado Integrado em Engenharia Física

Incorporação de nanomateriais refletores de radiação solar em termolaminados de alta pressão para fachadas exteriores

por [Alexandra SANTOS](#)

Num contexto de aquecimento global e aumento das temperaturas, existe uma procura considerável a nível mundial de energia para sistemas de refrigeração. No avanço para edifícios energeticamente eficientes, a regulação passiva da temperatura, sem necessidade de consumo de energia e sem emissões de gases com efeito de estufa, é uma alternativa apelativa para o arrefecimento de edifícios. A radiação do infravermelho próximo (NIR) abrange cerca de 50% da energia solar total que chega à Terra, e a incorporação de materiais com alta refletividade no NIR, e que mantêm transparência no visível para evitar alterações visuais, em laminados de alta pressão (HPLs) para fachadas exteriores é uma abordagem promissora para diminuir as temperaturas atingidas. Neste trabalho, o efeito da incorporação de materiais refletores NIR, nomeadamente SiO_2 1 μm e 60-70 nm e TiO_2 50 nm, foi avaliado para a melhoria do desempenho óptico e térmico de HPLs de forma a reduzir as necessidades energéticas. A incorporação de materiais refletores no NIR no overlay e no papel decorativo de um HPL resulta na melhoria da refletância em comparação com um HPL padrão com alterações de cor satisfatórias. A produção de HPL com um Exterior grade film (EG) foi realizada com papel decorativo dopado com nanopartículas de SiO_2 , uma vez que levaram à maior melhoria de refletância. Apesar da amostra de 7.5 wt% exibir o melhor aumento da refletância no NIR e total em relação a um HPL padrão ($\Delta R_{\text{NIR}} = 37.4\%$ e $\Delta R_{\text{total}} = 31.6\%$), as alterações de cor obtidas são superiores ao *threshold* $\Delta E = 3$. Assim, o EG HPL dopado com 5 wt% de SiO_2 foi selecionado como a amostra ideal, considerando o aumento relativo da refletância ($\Delta R_{\text{NIR}} = 31.6\%$ e $\Delta R_{\text{total}} = 23.5\%$) e as alterações de cor, que foram satisfatórias ($\Delta E = 1.5$). Para

avaliar se a dispersão de nanopartículas em PMMA resulta numa melhor distribuição de partículas e o efeito nas propriedades ópticas de um EG HPL, uma dispersão de 5 wt% de SiO₂/PMMA foi incorporada no HPL. Isto resultou num aumento relativo da refletância no NIR e total de 23.5% e 22.9% com mudanças de cor aceitáveis ($\Delta E = 1.5$). O espectro de FTIR dos HPLs dopados exibiu absorbância/emissão significativa na janela de transparência atmosférica (ATW), indicando um potencial para libertação do excesso de calor. Este estudo permitiu-nos alcançar resultados favoráveis relativamente à incorporação de materiais reflectores NIR em HPLs, abrindo a porta para outras aplicações.

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Glossary

HPL	High pressure laminates
NIR	Near infrared radiation
ATW	Atmospheric transparency window
VIS	Visible radiation
UV	Ultraviolet radiation
PMMA	Poly(methyl methacrylate)
PVDF	Polyvinylidene fluoride
EG	Exterior grade
CEN	European Committee for Standardization
PDRC	Passive daytime radiative cooling
CIE	Commission Internationale de l'Eclairage
FTIR-ATR	Attenuated total reflectance Fourier transform infrared

Chapter 1

Introduction

1.1 Surforma

The present study was conducted within the framework of a curricular internship carried out at Surforma. Surforma is integrated in the Sonae Indústria group, which has over 60 years of innovation and leadership in the furniture, construction and interior design sectors. Surforma aims to create a unique identity and lead in the production and distribution of laminates and compacts for the furniture, construction and decoration industries. Surforma offers solutions that are functional, innovative, with high quality and unique designs, adding great value to projects ranging from the most traditional to the boldest [1].

Surforma is investigating the viability of introducing a new product for outdoor applications, that has the aspect of a conventional high-pressure laminate, with the advantage of promoting energy efficiency by displaying solar reflective properties, thus reducing heat gains (Fig.1.1).

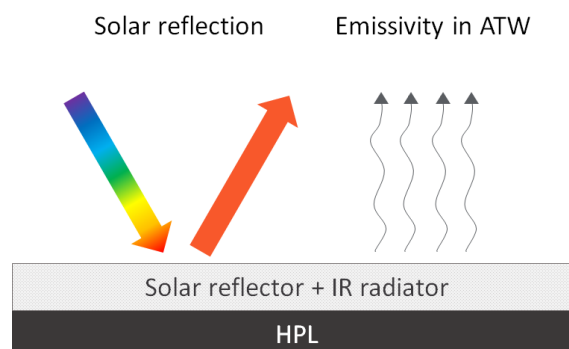


FIGURE 1.1: Solar reflective structure.

1.2 Context and Motivation

Under the background of global warming and populational growth, there is a considerable worldwide energy demand for cooling systems. According to the EU report in 2018 [2], about 63.6% of the total energy consumption and greenhouse gas emissions of Europe attributed to buildings is used for heating and cooling.

The biggest contributor to overheating in buildings is the absorption of incoming solar radiation, which is influenced by the façade's materials. Part of the solar radiation that strikes a surface is absorbed and transferred as heat [3], causing a temperature rise in the surface. Therefore, large energy consumption is required to ensure the thermal comfort of residents.

Furthermore, one of the leading causes of ageing and degradation of coatings is temperature, and an indirect benefit of diminishing overheating is limiting the cyclic thermal expansion of the structures, promoting coatings with good resistance and endurance. This results in greater reliability of their characteristics over time, reducing the maintenance operations and costs [3].

The materials employed in the envelope of buildings are critical in the urban thermal balance, as they absorb solar radiation and dissipate part of the accumulated heat through convective and radiative processes to the atmosphere increasing ambient temperature [4]. Therefore, the technical characteristics of these materials are determinant in the energy consumption and comfort conditions of buildings [4].

Moving towards energy-efficient buildings, passive temperature regulation, not requiring any power input and with no contributions to greenhouse gas emissions, is an appealing alternative to mitigate the cooling requirements of buildings [3]. A promising technique to mitigate the large cooling needs is the use of coatings with high solar reflectivity and high spectral emissivity [4, 5]. By lowering the solar absorption, reflective coatings that reflect an extensive portion of the incident solar radiation reduce the thermal gains of a surface (Fig. 1.2). In particular, embedding materials with high reflectivity and emissivity in the near-infrared (NIR) spectrum, which comprises nearly 50% of the solar energy, in high-pressure laminates (HPL) for exterior façades, can lead to an improvement in indoor cooling performance by lowering solar absorption during the daytime, thus reducing overheating, without affecting the colour. It is worth noting that there is an almost total absence of existing academic research addressing high-pressure laminates with solar reflective properties and this thesis aims to address this major gap.

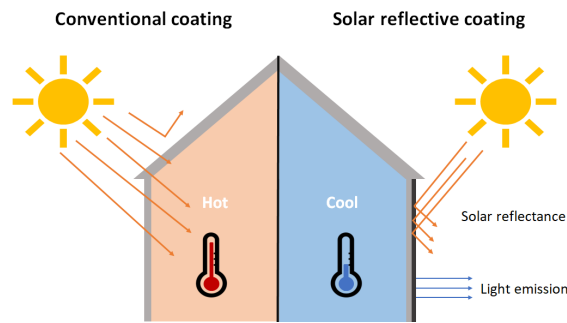


FIGURE 1.2: Conventional vs. solar reflective coating.

1.3 Objectives

The present work aims to assess the effect of the incorporation of NIR reflective materials on high-pressure laminates for the improvement of the energy efficiency of façades. This objective was carried out by evaluating the optical and thermal performance of high-pressure laminates with the incorporation of NIR reflective materials. As such, the objectives to achieve included:

- Comprehend thoroughly the composition, qualities and applications of HPL;
- Understand in detail the production process of high-pressure laminates;
- Investigate how and where in the production process should the NIR reflective materials be incorporated;
- Select suitable NIR reflective materials, considering both reflectance, emissivity and colour;
- Evaluate the optical properties of the HPL containing NIR reflective materials, through reflectance and colour measurements;
- Implement a thermal measurement setup to determine the thermal behaviour of standard HPLs and HPL with solar reflective properties.

1.4 Overview

The present work is focused on the development of High-Pressure Laminates with NIR reflective properties and is divided into five chapters. In the first chapter, an introduction to this work is presented, along with information about the company, the context,

motivation and objectives to achieve. The second chapter provides a characterization of High-Pressure Laminates and an overview of the current state of the art regarding NIR reflective materials, from their characteristics to their applications. The third chapter describes the materials and methods for the incorporation of NIR reflective materials along with the production process of HPL. The techniques employed for the characterization of the optical and morphological properties of the HPL with embedded NIR reflective materials as well as the methods applied for the control of the final product are detailed. The fourth chapter discusses and critically analyses the results obtained from the experimental techniques. Lastly, chapter five provides the main conclusions of the study developed, as well as suggestions for further work.

Chapter 2

State of the art

2.1 High-Pressure Laminates

Decorative high-pressure laminates (HPLs) are defined by the standard EN 438 as sheets consisting of a decorative surface layer and core layers bonded together by a high-pressure process, with typical values of temperature above 120 °C and pressures above 5 MPa [6]. HPLs are practical and durable, with great physical and chemical resistance, as well as being simple to work and maintain, making them attractive for the construction and furniture industries. These panels are typically applied as a superficial solution, for their selected properties such as fire and flame resistance, antibacterial, antifungal, and anti-fingerprint, or for their aesthetic characteristics, such as colour, glossiness, and opacity [7].

Aesthetic-wise, HPLs can be classified into three groups: printed, unicolour, and metallic (Fig. 2.1). Printed HPLs are characterized by the use of decorative papers with patterns, including wood and tiles, among others. The use of printed decorative paper requires an overlay in the laminate buildup to guarantee the resistance of the final product. Unicolour HPL uses decorative paper with a single solid colour, and, due to its higher grammage, has a natural resistance to abrasion. Finally, metallic HPL use a metallic sheet instead of a decorative paper sheet and can be presented with different textures and patterns.

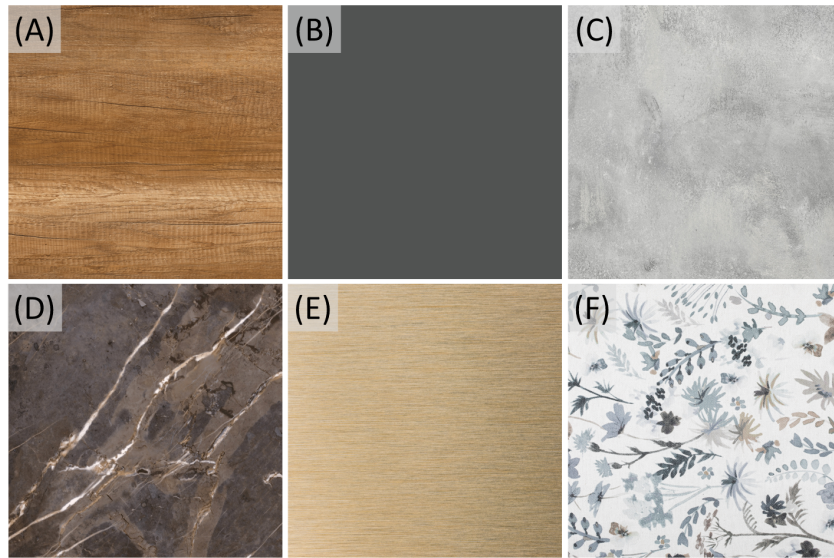


FIGURE 2.1: Examples of decorative HPL: (A) *Canyon Monumental Oak*, (B) *Dark Grey*, (C) *Artwall Grey*, (D) *Carnico*, (E) *Gold Aluminium* and (F) *Taupe Leaves*. From Ref. [7].

In addition to being available in a wide variety of colours, patterns and surface finishes, HPLs have several attractive qualities such as resistance to wear, scratching, impact, moisture, heat and staining. With high mechanical resistance and durability, HPLs are also easy to clean and maintain.

Being a versatile product, HPL are suitable for use on horizontal and vertical surfaces. High-pressure laminates are frequently applied indoors for floor covering, walls, and for decorative purposes, including table tops, kitchen countertops, doors, etc. This product can also be employed for exterior applications, such as façades, requiring reinforcements to endure large thermal amplitudes and radiation [8]. Some applications of HPL in different spaces are shown in Figure 2.2.



FIGURE 2.2: Examples of some applications of HPLs. From Ref. [8].

2.1.1 Composition and materials

HPLs are constituted by several layers of impregnated paper, particularly, by a core of kraft paper sheets, and by the outer layers of decorative paper and an optional overlay, bonded by a high temperature and pressure process. An illustration of the constitution of a standard HPL is depicted in Figure 2.3.

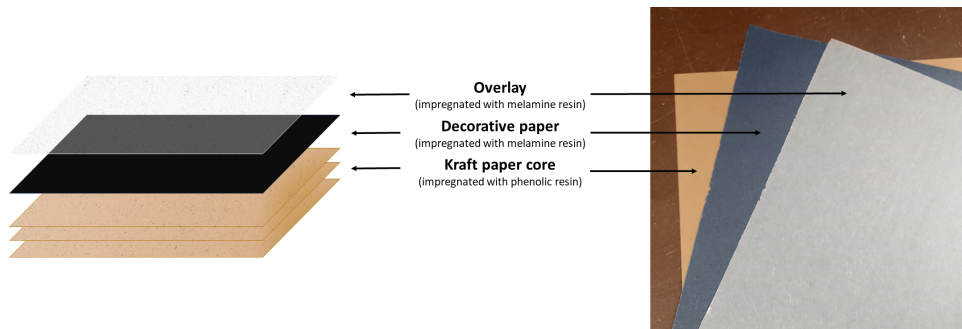


FIGURE 2.3: Constitution of a standard HPL: kraft paper, decorative paper and overlay.

Kraft paper consists of unbleached fibrous materials, that, due to its high grammage is impregnated with phenolic resin, which grants physical and mechanical resistance to the product. Kraft paper is robust and resistant, and the sheets are stacked until the desired thickness is achieved, thus composing the core of the HPL.

The decorative paper, impregnated with melamine resin, is made of high-quality bleached cellulose fibre, so it can be printed or dyed with various patterns, including wood, tile, stone and personalized prints, providing the aesthetic characteristics of the laminate.

The overlay is a transparent paper, and as a result of its high porosity, it can absorb a large amount of resin (in this case, melamine resins). Owing to its transparency, the overlay is applied on top of printed decorative paper, providing a greater abrasive resistance without altering the appearance of the laminate [9].

Impregnation is a process where parched paper is saturated with liquid resin. Melamine and phenolic resins are thermoset resins used for paper impregnation, and the type of resin used depends on the intended functions of the layers. The kraft paper sheets are impregnated with phenolic resin, while the decorative paper and the overlay are impregnated with melamine resin. During pressing, under the effect of high temperatures and pressures, phenolic resins confer thermosetting properties to the kraft paper, rendering it a homogeneous material. Therefore, the core layers of the laminate are impregnated with phenolic resins. The superficial layers of a HPL are impregnated with melamine resin, as this resin confers transparent, rigid, and light-resistant coatings.

The layers that compose the laminate are bonded through the curing of the thermoset resins, which occurs under simultaneous application of heat ($\geq 120\text{ }^{\circ}\text{C}$) and pressure ($\geq 5\text{ MPa}$), leading to a rigid, homogeneous, and non-porous final product. During the pressing process, the high pressures and temperatures induce irreversible chemical bonds in the resin, guaranteeing the stability of the final product without the need for additional chemicals. Since its durability relies on thermosetting, the resin content substantially affects all of these properties. The final product is attached (glued) to substrates such as MDF (medium-density fibreboard) or particle board, that provide a stable, durable, and economical base.

2.1.2 Production process

The HPL manufacturing process comprises several successive steps: impregnation, pressing, cutting and sanding, and visual inspection (Fig. 2.4) [10].

The process starts with the impregnation of kraft and decorative paper with phenolic and melamine resin, respectively. The paper sheets are then dried and cut to the appropriate sizes for the press. Before the pressing, the different types of paper are stacked in distinct layers to form the laminate. For a singular laminate, this step starts by stacking the established number of impregnated kraft sheets (for the intended thickness), followed by the decorative paper and optional overlay, ending with a metal finishing plate, which will add the desired aspect/texture to the laminate.

Once assembled, the stack of paper is placed inside the plates of the press. The industrial press has several apertures to enable the production of a large number of laminates simultaneously. The temperature, pressure and duration of the pressing cycle depend on the type of product to be manufactured, the resins used and the intended thickness. Usual values are from 5 to 10 MPa for pressure, 120° and 150°C for temperature, and 20 to 60 minutes for the duration of the pressing cycle. While the laminate is inside the press, the pressure and temperature applied induce the curing of the resins, as the liquefied resins penetrate the cellulose fibres, creating strong and irreversible bounds, leading to the formation of a three-dimensional network that prevents the softening of the product. After pressing, the laminate cools down inside the press.

At last, the product is cut in the correct dimensions, and the counterface is sanded to make it rougher, facilitating its application on a substrate. The process ends with a visual inspection for any kind of defects.

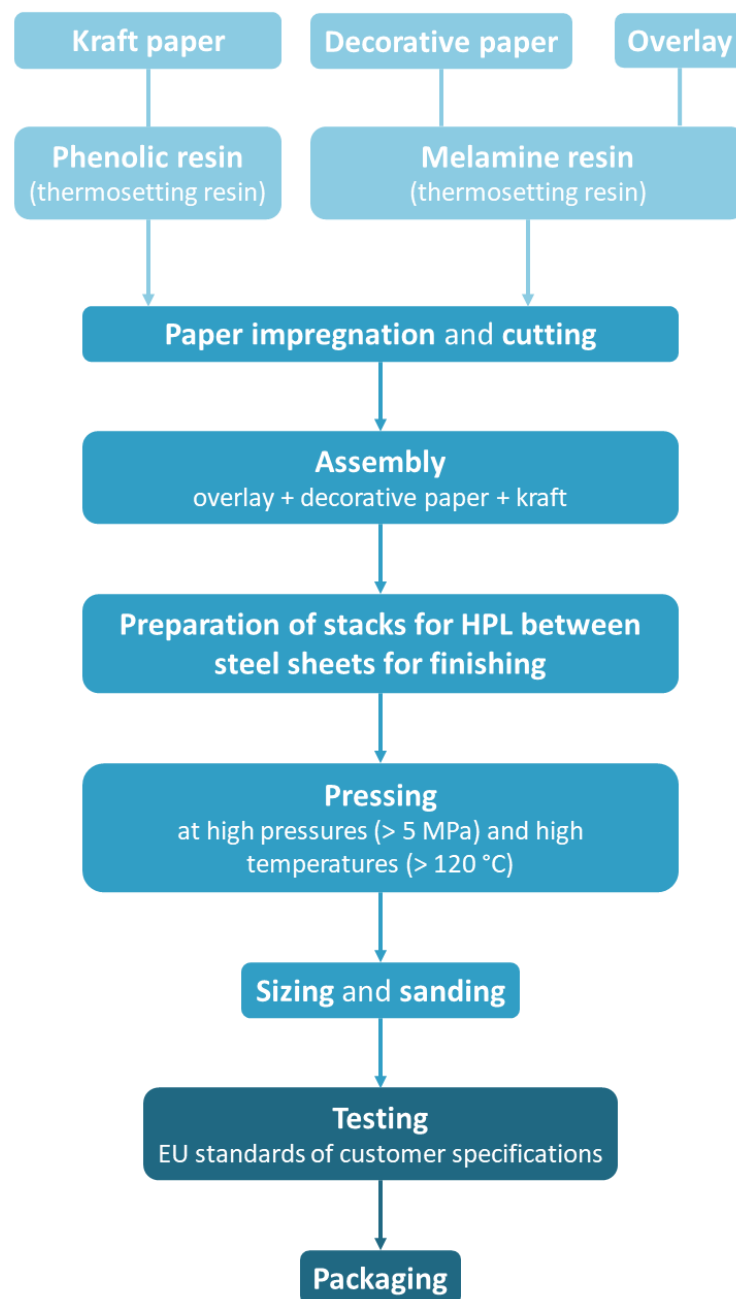


FIGURE 2.4: Production process of an HPL.

2.1.3 Exterior-grade compact laminates

Exterior-grade (EG) compact laminates are characterized by having high tensile strength, high impact resistance, thermal shock resistance, and resistance to weather and corrosion. They are available in a variety of decorative colours, retaining high resistance to colour

alterations and ageing when used in outdoor spaces [11]. The surface layer (upper decorative layer) of an exterior grade laminate is similar to one of a conventional HPL, with an additional appropriate outer layer or coating to enhance its weather and light-protecting properties (Fig. 2.5).

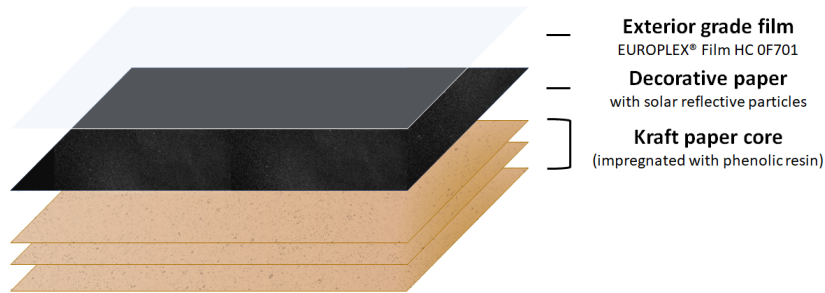


FIGURE 2.5: Constitution of an Exterior grade HPL: exterior grade film, decorative paper and kraft paper.

The EG film used in this study, EUROPLEX® Film HC 0F701, is a transparent, coextruded PMMA film with great resistance to weather and abrasion, used for both decorative and protective purposes. Its colourless aspect preserves the colour and characteristics of the decorative face applied on the back of the film. The back side of the film is constituted by a PMMA resin, ensuring excellent chemical adhesion to melamine resin, thus allowing good bonding to thermosetting materials, such as high-pressure laminate panels. The high-performing UV absorber package is present in the intermediate layer. The top side, constituted by PVDF, grants remarkable weather and chemical resistance properties. This 3-layer design allows state-of-the-art UV protection and outstanding performance in long-term outdoor weathering without the risk of colour change or yellowing. HPL with EUROPLEX® HC Film 0F701 as a surface coating display surface hardness levels of level 5 as per EN 438-2.25:2016 [12, 13].

2.1.4 Standard EN 438

The most recent version of standard EN 438 was reviewed in 2016 by the European Committee for Standardization (CEN) and is divided into 7 distinct parts. The first part, EN 438-1, gives an introduction and defines general information about high-pressure decorative laminates. The second part, EN 438-2 [6], states the procedures to apply in each test for the determined HPL properties. The standard for Exterior-grade Compact laminates, namely EN 438-6 [6], specifies the requirements for standard and flame-retardant

laminates aimed for outdoor use, under weather conditions such as direct sunlight, rain and frost.

The European standard EN 438-2 defines all the tests, as well as the parameters required to determine the properties and performance of high-pressure decorative laminates in internal and external applications (e.g. construction, transport, furniture, flooring, etc.). For each property, the acceptable minimum requirements are established, and applying EN 438-2 is a way to guarantee the quality control of the products [6]. For recurrent quality control, only a few of those are applied, in particular resistance to immersion in boiling water, formability and resistance to blistering, resistance to surface wear (abrasion resistance), and resistance to scratching. All the stated characterization tests are fundamental to evaluate the material's behaviour when exposed to extreme conditions.

The requirements for Exterior grade laminates are stated in EN 438-6 and are divided into physical properties and weather resistance requirements. The physical properties are assessed through the resistance to wet conditions, dimensional stability at elevated temperatures and resistance to impact by a large-diameter ball test. The weather resistance tests evaluate the behaviour of Exterior-grade laminates in relation to degradation of the surface, colour fading and reduction of mechanical properties, due to exposure to external conditions, and include the resistance to climatic shock, resistance to UV light and resistance to artificial weathering tests [11].

The characterization methods employed in this study regarding EN 438, as well as the requirements for each of them, are detailed in section 3.

2.2 Nanoparticles for cooling efficiency

The typical spectrum of the solar irradiance on the earth's surface can be divided into different regions depending on the energy of the electromagnetic waves (Fig. 2.7). Nearly 52% of the total solar energy is radiated in the near-infrared (NIR) fraction of light (780–2500 nm), which is behind the heat build-up. The visible (VIS) portion of light (380–780 nm) contains approximately 43% of the total solar energy and determines the colour characteristics. The last 5% of the solar radiation corresponds to the ultraviolet spectrum (UV, < 380 nm) [3, 5, 14].

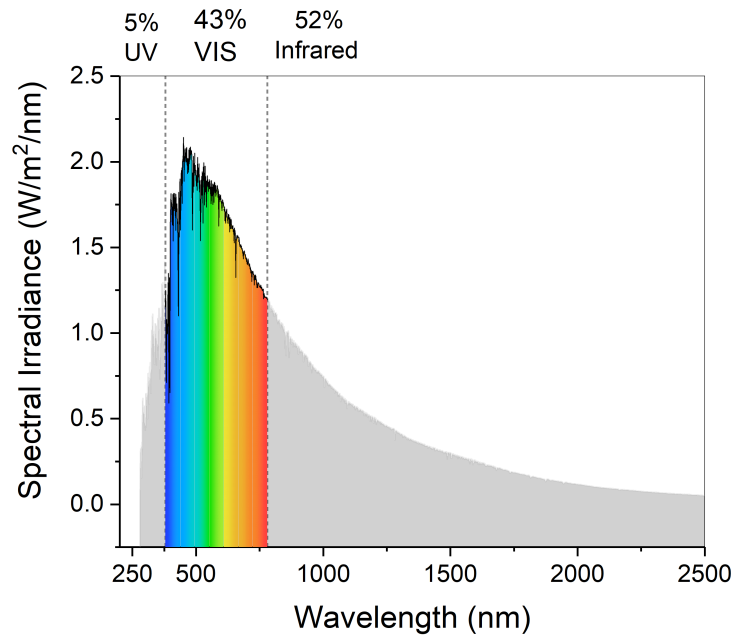


FIGURE 2.6: Spectrum of solar irradiance according to ASTM G173-03. Data from Ref. [15].

Solar reflective coatings are an extremely promising approach for passive cooling applications, contributing to achieve energy efficiency by reducing the energy demand for cooling in buildings, not requiring any energy input to operate, as well as being environmentally friendly and cost-effective [16, 17]. Nevertheless, the exterior appearance of a solar reflective coating is a fundamental factor to consider. To achieve high reflectance in the solar spectrum, most solar reflective coatings are white or silver, limiting the aesthetic characteristics of a structure. Transparency is advantageous and versatile for practical applications, allowing the preservation of the original colour/appearance of the structure on which the coating is applied. Therefore, a coating that is transparent in the visible spectrum and reflective in the non-visible solar range can be a satisfactory solution for various practical applications [18, 19]. Thus, and since NIR radiation accounts for approximately half of the total solar energy reaching the Earth, to mitigate the increase of indoor temperature, it is critical to develop the ability to reflect radiation in this spectral region [3, 20]. NIR reflective materials do not have electronic transitions for wavelengths above 700 nm [14], promoting a diffuse reflection of incident NIR wavelengths in this region [21]. As a result, the amount of energy absorbed by the building is reduced, minimizing the surface's temperature, which is a decisive factor for the reduction of thermal gains and overheating in buildings [3, 22].

Nanomaterials hold key characteristics that make them appealing and suitable for applications in diverse fields, from engineering, energy, technology, pharmaceutical, and agriculture, among others. Nanotechnology has a significant role in the improvement and development of materials for the construction sector, especially moving towards green, smart and efficient buildings [23, 24]. There is widespread research focused on improving the NIR reflectance of materials, aiming for novel effects and functional devices. Aside from their use derived from their reflective properties, nanomaterials can potentially confer supplementary benefits to construction materials, including increased durability, self-cleaning features and improved scratch resistance of coatings [23].

2.3 Passive daytime radiative cooling

Passive daytime radiative cooling (PDRC) is a passive and sustainable cooling technology that releases heat directly to outer space through thermal radiation. It is based on the large temperature difference between the Earth (300 K) and outer space (3 K), taking advantage of the transparent atmospheric window (ATW) between wavelengths of 8 and 13 μm . Recently, daytime radiative cooling has been appealing as an energy-saving and environmentally friendly technique for cooling applications, considering its demonstrated sub-ambient cooling effect under direct sunlight [16].

In the atmospheric transparency window, the radiative emission of the atmosphere is very weak, transmitting about 87% of the outgoing radiation from the earth [25, 26]. The ATW coincides with the peak thermal radiation of a black body defined by Plank's law at the ambient temperature (at around 300 K), enabling passive cooling for a terrestrial body at the ambient temperature by eliminating heat via radiative emission through the atmospheric window [25]. Radiative cooling can then be achieved by creating an imbalance between the heat radiated outwards through the transparency window, and the absorbed radiation from the environment, passively cooling down the surface below the ambient temperature [27].

To achieve passive radiative cooling the coating should strongly reflect incoming radiation in the solar spectrum to avoid heating, with a simultaneous high emittance through the ATW (Fig. 2.7) to maximize thermal radiation to the surroundings [28, 29]. Therefore, the heat dissipation of the structure should overpower the heat absorption, with a reflectance higher than 88% of the solar radiation being needed [27].

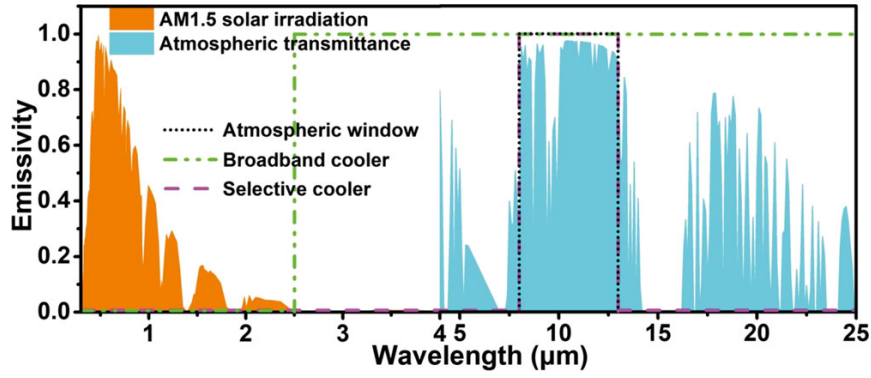


FIGURE 2.7: Spectral emissivity of a radiative cooler (with the backgrounds under AM1.5 solar irradiation and atmospheric transmittance) and atmospheric transparency window. From ref. [30].

The net cooling power, P_{net} of a surface corresponds to the net power outflow of the surface, as a function of its temperature, and is dependent on the solar radiation, the coating, the atmospheric thermal radiation and nonradiative heat transfer [16, 28, 31, 32], being expressed as:

$$P_{net}(T) = P_{rad}(T) - P_{atm}(T_{amb}) - P_{solar} - P_{nonrad} \quad (2.1)$$

where $P_{rad}(T)$ is the radiative power of the coating, $P_{atm}(T_{atm})$ is the absorbed power from the incident atmospheric thermal radiation, P_{solar} is the solar radiation absorbed by the coating and P_{nonrad} is the nonradiative power density. The heat exchange processes on the surface of PDRC are illustrated in Figure 2.8.

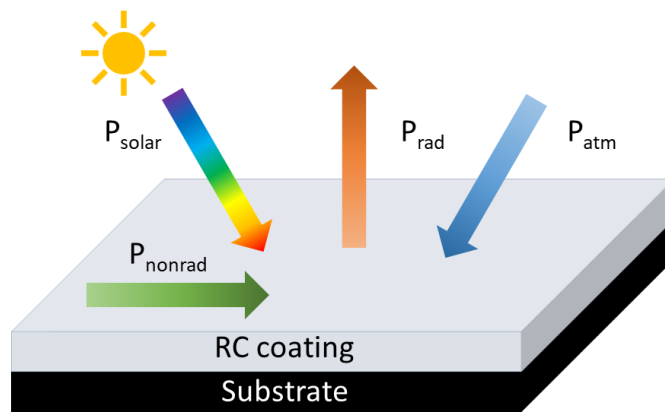


FIGURE 2.8: Schematic diagram of the heat transfer processes of PDRC coatings. P_{atm} and P_{solar} are the absorbed powers from the atmospheric and solar irradiations, respectively. P_{rad} is the thermal radiation power of the PDRC coating. P_{nonrad} denotes the nonradiative heat transfer processes between the coating and ambient environment.

In equation 2.1, $P_{rad}(T)$ is the radiative power of the coating:

$$P_{rad}(T) = 2\pi \int_0^{2\pi} \sin \theta \cos \theta d\theta \int_0^\infty I_{BB}(T, \lambda) \epsilon(\lambda, \theta) d\lambda \quad (2.2)$$

where $I_{BB}(T, \lambda) = (2hc^2)/(\lambda^5)[1/(e^{hc/(\lambda k_B T)} - 1)]$ indicates the spectral radiation of a blackbody at temperature T , λ is the wavelength, h is Plank's constant, k_B is the Boltzmann constant, c is the speed of light and $\epsilon(\lambda, \theta)$ is the angular emissivity of the radiator.

P_{solar} quantifies the solar radiation absorbed by the coating and can be expressed as:

$$P_{solar} = \int_0^\infty I_{AM1.5}(\lambda) \epsilon(\lambda, \theta) d\lambda \quad (2.3)$$

where $I_{AM1.5}$ is the solar illumination intensity according to the AM1.5 standard solar spectrum distribution (solar radiation = 1000 W m⁻²) [15].

According to Kirchhoff's law, in thermodynamic equilibrium, the absorptivity at a certain wavelength and direction is equal to the emissivity at that same wavelength and direction [33]. The absorbed power from the incident atmospheric thermal radiation, $P_{atm}(T_{atm})$, is given by:

$$P_{atm} = 2\pi \int_0^{2\pi} \sin \theta \cos \theta d\theta \int_0^\infty I_{BB}(T_{atm}, \lambda) \epsilon_{atm}(\lambda, \theta) \epsilon(\lambda, \theta) d\lambda \quad (2.4)$$

where $\epsilon_{atm}(\lambda, \theta)$ is the atmospheric emissivity, given by $\epsilon_{atm} = 1 - t(\lambda)^{1/\cos \theta}$, $t(\lambda)$ being the atmospheric transmittance in the zenith direction.

P_{nonrad} is the nonradiative power density induced by thermal conduction and convection between the environment and the coating and is given by $P_{nonrad} = h_c(T_{amb} - T)$, where h_c is the non-radiative heat transfer coefficient, derived from the conductive and convective heat exchange between the radiator and surrounding media, and $h_c = h_{cond} + h_{conv}$.

For a material with a certain colour/aesthetic, the coating should lower the superficial temperature as extensively as possible while preserving its visual characteristics [27]. For this reason, given the constraints posed by compromising the VIS reflectance for colour preservation purposes, we do not seek to achieve an equilibrium temperature that is below the ambient [27]. Taking this into account, we aim to apply the radiative cooling fundamentals to improve the optical and thermal properties of the material.

2.4 Materials for solar reflective and radiative cooling applications

Early studies used metal reflective layers (silver and aluminium) to achieve high solar reflectance [34–37]. However, long-term outdoor exposure leads to oxidation of the metal and discomfort to the human eye, limiting the possible applications of these structures. The use of metal-based solar reflective layers also restricts the colour of the structure [38] and, to improve and diversify the aesthetic properties, it is essential to develop coatings that do not alter the original characteristics of the material.

Metal oxide materials, such as titanium dioxide (TiO_2), zinc oxide (ZnO), and zirconium dioxide (ZrO_2), are frequently used as solar reflective layers due to their high refractive indexes and shielding effects toward ultraviolet light [26, 39, 40]. The high surface area of metal oxide nanoparticles makes them appealing for applications in coatings [41]. Nevertheless, these materials display moderate bandgaps and the strong solar absorption in the ultraviolet band still restricts the radiative cooling performance [42]. In this regard, high-energy bandgap materials, including silica (SiO_2), alumina (Al_2O_3) and barium sulfate (BaSO_4), have been proposed as reflective or emission layers to minimize the absorption of solar radiation [43–46].

In this section, the most promising materials for the improvement of solar reflectance and emissivity in the ATW will be detailed.

2.4.1 Titanium dioxide

Titanium dioxide (TiO_2) is a white pigment with high opacity, excellent covering power and resistance to colour change, being widely applied in coatings formulation for the improvement of the quality, durability and brightness of the coating. Additional properties such as low cost, non-toxicity, optical transparency, chemical stability and good thermal performance are appealing for eco-friendly applications, including in construction materials [23].

The behaviour of TiO_2 materials depends on their electronic and optical properties, particle size, morphology, and crystalline structure. TiO_2 particles strongly scatter solar radiation from the visible to the NIR range, as well as having extinction absorption in the atmospheric window band [47]. Given that TiO_2 has a solar reflectance of roughly 87% [48] and active UV protection, TiO_2 in the Rutile phase (its most stable modification) is

regarded as one of the most effective and commonly selected materials for solar reflective applications. TiO_2 has a higher refractive index compared to other white materials (e.g., BaSO_4 , ZnO) [49], making it appealing for applications as a NIR reflective material. Compared to materials with lower refractive indexes, the application of TiO_2 leads to higher spectral reflectance across the solar spectrum (with the exception of the UV region) [50], as it efficiently scatters and reflects light because of the difference in refractive indices between TiO_2 and the matrix [51]. However, considering its wide bandgap, the intrinsic absorption in the ultraviolet range limits its radiative cooling performance [21].

As an example, Bao et al. [26] designed a nanoparticle-based double-layer coating with selective radiative properties (Fig. 2.9). The coating with a TiO_2 reflective layer and a SiO_2 emissive layer reached a solar reflectance of 90.7%

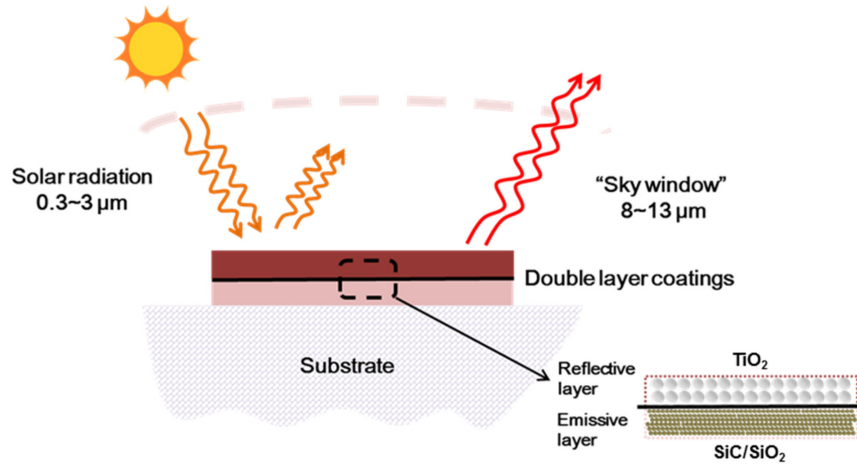


FIGURE 2.9: Schematic of a double-layer coating design for efficient radiative cooling. From ref. [26].

2.4.2 Silicon dioxide

Silicon oxide (SiO_2), or silica, is frequently utilized for radiative cooling structures as a remarkable spectral selective material. SiO_2 is transparent in the solar spectrum and highly emissive in the infrared spectrum (in the ATW), as well as being low-cost and abundant, making it an excellent material for radiative cooling applications [52].

The extinction coefficient of SiO_2 is almost zero over the whole solar radiation spectrum [53] which is favourable for achieving radiative cooling [54, 54]. This also indicates that this material is transparent to solar radiation [55].

Silicon (Si)-based functional groups, including Si-O-Si have stretching vibration frequencies corresponding to IR regions, promoting strong thermal absorption and emission

in the mid-IR range (8-20 μm), which covers the atmospheric transparency window [56]. The Si–O–Si bonds of silica along with the strong peak in its absorptivity near 9 μm (due to its phonon–polariton resonance) demonstrate a great promise as an ideal selective thermal emitter, with high solar reflectance and strong thermal emission [57].

As an example, Xue et al. [58] fabricated a hierarchically structured porous film with hydrophobic SiO_2 nanoparticles and P(VDF-HFP). The film presented remarkable radiative cooling performance, achieving 10.3 $^\circ\text{C}$ cooling under direct sunlight, and the SiO_2 particles enhanced the mid-infrared emissivity of the film.

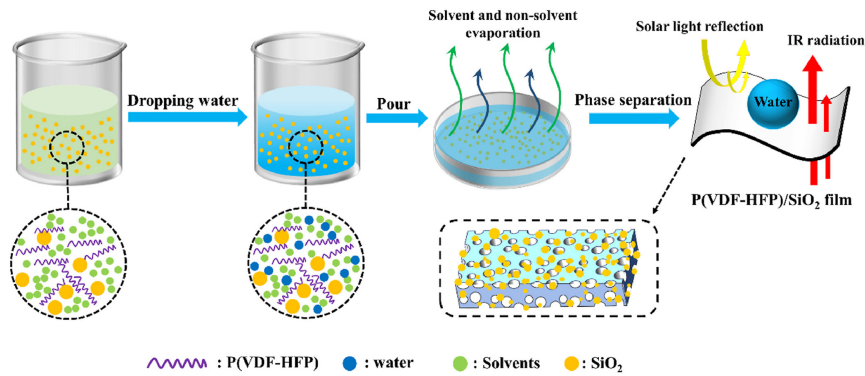


FIGURE 2.10: Fabrication of hierarchically structured porous P(VDF-HFP)/ SiO_2 film. From Ref. [58].

2.4.3 Polymers

A growing interest in polymer-based PDRC coatings, films and paints has been observed, considering their potential for mass production, low cost, and applicability to various systems. Polymers have superior transmittance and promising infrared emission behaviours, which are ideal for radiative cooling applications [59].

The infrared absorption and emission in polymers are caused by the vibrations of functional groups, which determine their infrared emission behaviours. The infrared fingertip region of polymers, also known as the crowded region, ranging from 6.7 to 16.7 μm of the electromagnetic spectrum, overlaps the ATW and is responsible for the high thermal mid-infrared emittance. Therefore, the infrared emission from a large number of polymers can contribute for radiative cooling, provided that these polymers are highly reflective, highly transparent, or non-absorbing over the solar spectrum.

Polyvinylidene fluoride (PVDF) and poly(methyl methacrylate) (PMMA) are polymers frequently employed for PDRC structures. Attenuated total reflectance Fourier transform infrared (FTIR-ATR) spectra of PVDF and PMMA films show groups, such as

C–H and C–F for PVDF and C–H, C=O and C–O for PMMA [59], with bending vibrations in the crowded region, i.e. the atmospheric window. The intrinsic absorption of polymers, with functional groups that overlap with the atmospheric transmittance window [59, 60], are suitable for radiative cooling applications, in view of exhibiting high emittance (above 95%) in the ATW [61].

Wang et al. [62] report a hierarchically porous array PMMA film (Fig. 2.11) with high reflectance (95%) and infrared thermal emittance (98%). Outdoor experiments under solar intensity of 900 W/m^2 show that the film achieves sub-ambient cooling of 6.0°C to 8.9°C during midday with an average cooling power of 85 W/m^2 . Huang et al. [63] proposed a hierarchically structured PVDF/PDMS porous radiative cooling film with high sunlight reflectance (97%) and thermal-infrared emittance (96%). Under direct sunlight, the film exhibits an average sub-ambient temperature drop of 12.3°C .

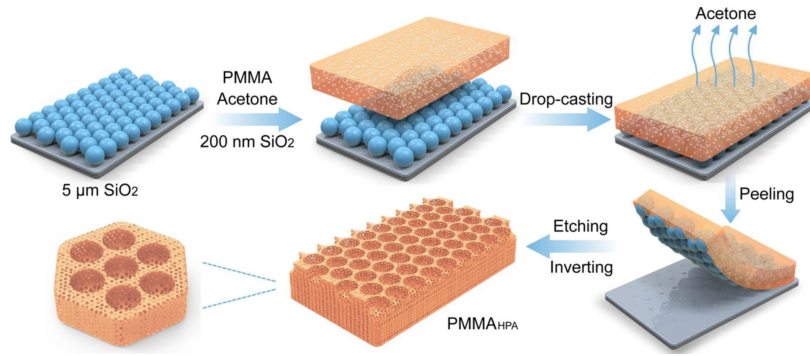


FIGURE 2.11: Schematic illustration of the fabrication of PMMA_{HPA} with a hierarchically porous array. From Ref. [62].

Furthermore, Aili et al. [59] studied the influence of PVDF and PMMA films placed on a silver mirror on the daytime cooling performance. It was determined that the average emissivity in the ATW of the PVDF film was 91%, whereas the PMMA film had a slightly lower emissivity of 89%. The PVDF film also showed lower solar absorptivity and the daytime cooling performance is superior to the results with the PMMA film, with peak sunlight sub-ambient cooling by 6°C in contrast to 4°C .

2.5 Superficial properties

2.5.1 Solar reflectance

Solar reflectance (R_{solar}) measures the ability of a material to reflect the incoming solar radiation and designates the total reflectance of a surface, considering the hemispherical

reflectance of radiation, integrated over the solar spectrum, including specular and diffuse reflection. It is measured on a scale of 0 to 1 [4, 64].

R_{solar} is expressed as the ratio of the reflected solar intensity to the integral solar intensity for wavelengths (λ) between 0.3 and 2.5 μm [28], according to:

$$R_{solar} = \frac{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_{solar}(\lambda) R(\lambda) d\lambda}{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_{solar}(\lambda) d\lambda} \quad (2.5)$$

where $I_{solar}(\lambda)$ represents the ASTM G173-03 global solar intensity spectrum at AM 1.5 and $R(\lambda)$ is the spectral reflectance of the coating.

2.5.2 Thermal emittance

Thermal emittance (ε) is a measure of the ability of a surface to re-emit previously absorbed heat to the surrounding environment. It specifies how well a surface radiates energy away from itself as compared with a blackbody operating at the same temperature. Infrared emittance is measured on a scale from 0 to 1, representing the comparative/relative emittance with respect to a blackbody operating in similar conditions [4, 64].

The thermal emittance, ε_{ATW} , in the atmospheric transparency window is expressed as:

$$\varepsilon_{ATW} = \frac{\int_{8\mu\text{m}}^{13\mu\text{m}} I_{bb}(T, \lambda) \varepsilon(T, \lambda) d\lambda}{\int_{8\mu\text{m}}^{13\mu\text{m}} I_{BB}(T, \lambda) d\lambda} \quad (2.6)$$

where I_{bb} is the spectral intensity emitted by a standard black body at temperature T and $\varepsilon(T, \lambda)$ corresponds to the spectral emittance of the sample.

According to Kirchhoff's law, at thermal equilibrium, the change in NIR absorptance corresponds to an equal change in NIR emittance [62, 65]. To improve the PDRC performance in sub-ambient conditions, mid-infrared emittance, at 8 to 13 μm should be increased. As such, materials should be almost transparent in the solar spectrum to prevent solar absorption and heating and exhibit strong absorption in the atmospheric transparency window to emit more heat to the deep outer space [28].

2.5.3 Colour variation

Colourimetry is often used in many sectors as an indicator of changes in the material aspect. Besides being an aesthetic element, the colour of façades is a key element for durability, as darker coloured façades reach higher temperatures [66], contributing both to higher cooling demands and degradation.

The colour of a material depends on its characteristics and the properties of the light source as well as the illumination angle [67]. The Commission Internationale de l'Eclairage (CIE) system (Fig. 2.12) is a colourimetry system for precise colour measurement by standardisation of several factors that affect the perceived colour of a material [68]. The CIE colourimetric coordinates, lightness L^* (black-white), a^* (green-red) and b^* (blue-yellow) are used to analyze the colour coordinates of materials. Particularly, L^* is the lightness and darkness factor varying from 0 (black) to 100 (white), a^* is the red-green coordinate ranging from -60 (green) to +60 (red), and b^* is the yellow-blue coordinate ranging from -60 (blue) to +60 (yellow).

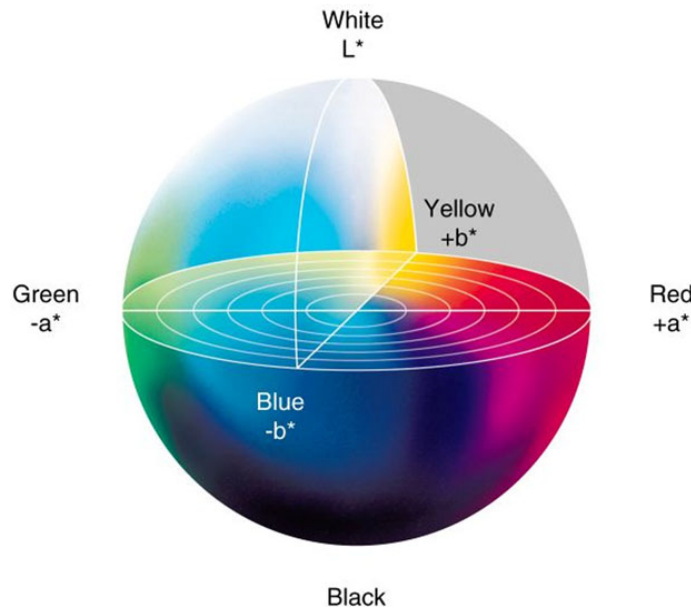


FIGURE 2.12: CIELAB colour system. From Ref. [69].

Colour differences are an essential parameter to assess how doping with solar reflective materials alters the structure's aesthetic, and are calculated as the Euclidean distance between two points in the three-dimensional space defined by L^* , a^* , and b^* . The global colour difference (ΔE^*), representing the colour difference between two samples, is expressed as [3]:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2.7)$$

where $\Delta L^* = L_1^* - L_0^*$ is the difference in lightness (with $\Delta L^* > 0$ indicating a lighter material), $\Delta a^* = a_1^* - a_0^*$ is the difference in red and green and $\Delta b^* = b_1^* - b_0^*$ being the difference in yellow-blue.

Perceptiveness	Total colour difference
Very perceptible	$\Delta E > 3$
Perceptible	$1.5 < \Delta E < 3$
Almost imperceptible	$\Delta E < 1.5$

TABLE 2.1: Colour perceptiveness.

Usually, $\Delta E^* = 1$ is the lowest colour difference the human eye can distinguish; however, considering the colour tolerances typical of manufacturing processes, in the present study, a threshold $\Delta E^* = 3$ will be considered for colour matching acceptance [3].

Chapter 3

Experimental procedures and characterization techniques

3.1 Materials

To optimize the solar reflectance of HPL, the use of different materials and sizes was evaluated.

A study carried out by Veloso et al. [70] observed that, for a set of particles with sizes ranging from 30 nm to <5000 nm, TiO₂ Rutile with 50 nm size presented the largest optical band gap, predicting that these nanoparticles would lead to the best improvements of the reflectance of the colourant. It was determined that, for this size range, the global reflectance maximum reached 20% for a TiO₂ with 50 nm particle size (compared to 13% for the standard colourant) for a 16% concentration. As such, TiO₂ Rutile 50 nm particles were selected for this study. To compare different types of particles in the same order of magnitude, SiO₂ 60-70 nm size particles were chosen. As for the study of different sizes of the same particle, SiO₂ 1 μ m size particles were selected as well.

Titanium dioxide rutile (50 nm particle size, 99.9+% purity) and silicon dioxide (60-70 nm particle size, 98+% purity) were purchased from US Nano [71] and SiO₂ (1 μ m particle size, 99% purity) was purchased from SINOENERGY [72]. In this study, the particles were utilized as received.

In order to study the influence of the type and size of the particles on the solar reflectance of the HPL, the three particles were dispersed in water under continuous stirring in different proportions to obtain different concentrations (1%, 2.5%, 3.75% and 5%). Water was selected as the dispersant for several reasons. If the particles disperse well

in water, it would be the optimal choice due to its low environmental impact, and being cost-effective and practical for large-scale applications.

For the manufacturing of the samples, black decorative paper was selected, since the black colour is the most critical for light absorption, any visual alterations are more easily identified and reflectance improvements would be the most significant. The manufactured samples had an area of $25.5 \times 25.5 \text{ cm}^2$ and a thickness of $\sim 0.3 \text{ cm}$.

3.2 Experimental procedure

A diagram depicting the experimental procedure applied for the incorporation of solar reflective materials in HPL and the characterization of the optical and thermal properties of the doped HPL is represented in Figure 3.1.

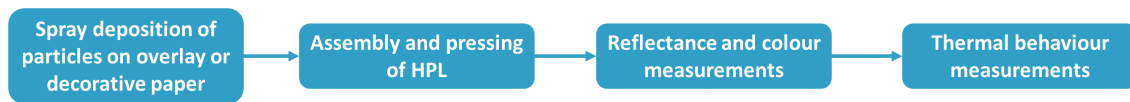


FIGURE 3.1: Experimental procedure for the incorporation of solar reflective materials in HPL.

In this study, three distinct types of samples were produced: on the first (Fig. 3.2a) the deposition of particles was performed on the overlay; on the second (Fig. 3.2b), the particles were deposited in the decorative paper, and no other optional layer was applied; and on the third (Fig. 3.2c) the particles were deposited on the decorative paper and an Exterior grade (EG) film was used as the outer layer.

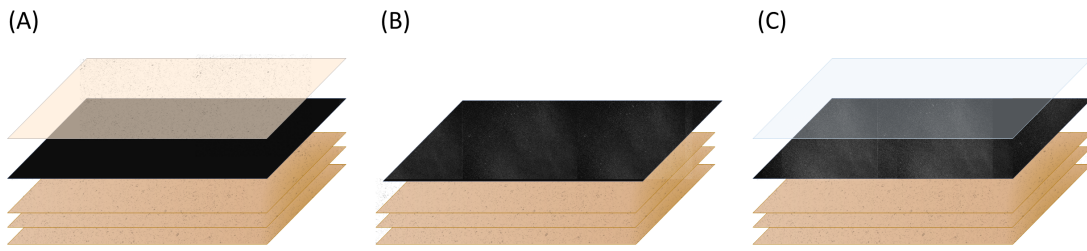


FIGURE 3.2: Different types of samples produced: (A) with deposition of particles in the overlay, (B) with deposition of particles in the decorative paper and without the use of optional layers, and (C) with deposition of particles in the decorative paper and use of Exterior Grade (EG) film.

3.2.1 Spray deposition of nanoparticles

Spray deposition is a technique easy to implement in the production process, scalable and cost-effective. Surforma has a spray deposition line (Figure 3.3) comprised of seven DEXTER 1.5 mm diameter nozzle spray guns, placed 28 cm above the substrate. The system moves horizontally and is connected to a 5 l container and a hot air dryer. Inside the container, the required amount of material (in mass) is added to the volume of water, under continuous stirring. Once the dryer reaches a temperature of 120 °C, the line can be turned on, starting the deposition. After reaching the end of the line, the spray guns are turned off and the hot air dryer dries the paper. Once the sheets are dry, they follow to the press for the assembly of the laminate.

The particles were incorporated in the outer layer of the HPL in order to attain the maximum solar reflectance performance. The deposition process was carried out both on the overlay and on the decorative paper.

The dispersion obtained with SiO₂ micro and nanoparticles was visually homogeneous. On the other hand, TiO₂ nanoparticles are not easily dispersed in water; thus, the dispersion for the spray deposition was not homogeneous. Furthermore, some TiO₂ nanoparticles accumulated at the bottom of the stirring system in the container, which further hints to a variation of the deposition from the intended one. Nano-sized TiO₂ has a significant tendency to agglomerate due to their large surface area, strong polarity and incompatibility in aqueous suspensions, making it challenging to achieve a stable dispersion. This problem is further aggravated with increasing particle-filling fractions [73, 74]. Thus, it is not possible to certify that the concentration deposited is the same as of the dispersions prepared.

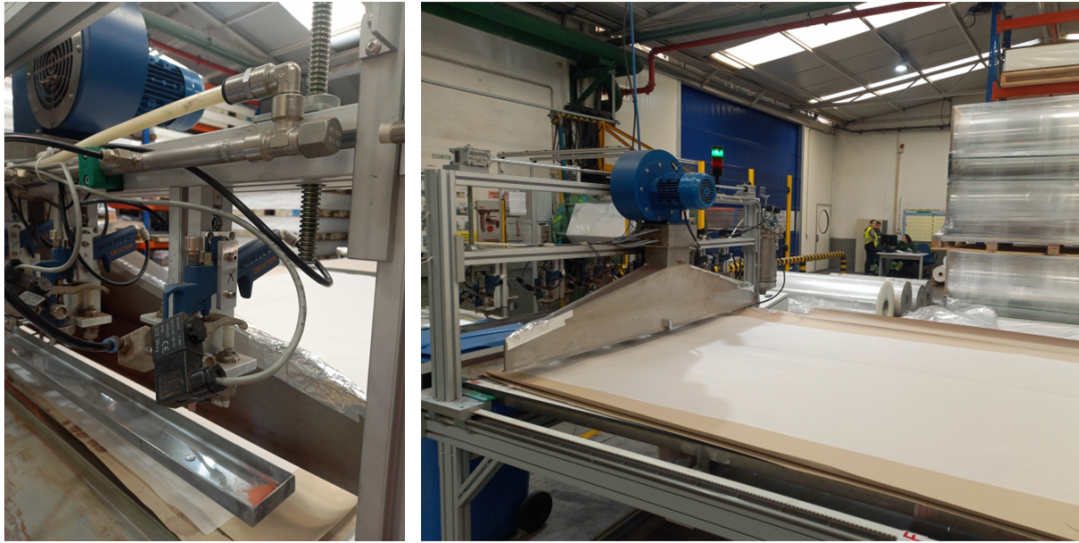


FIGURE 3.3: Spray deposition line at Surforma.

3.2.2 Manufacturing of High-pressure laminates in the test press

In each iteration of the press, it is possible to stack distinct laminates made with different finishing steel plates. For this purpose, the build-ups are separated with sheets of polypropylene, allowing to manufacture several and/or distinct laminates in a single pressing process. All the samples used in this work were manufactured in the test press (Fig. 3.4) available at Surforma.

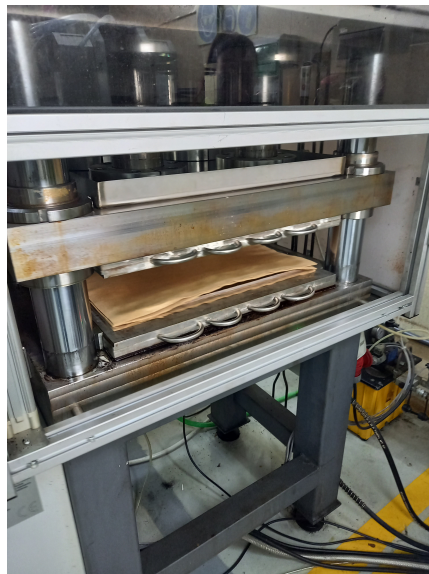


FIGURE 3.4: Test press at Surforma.

As referred in Chapter 2, the laminates are composed of a core of kraft paper, followed by a sheet of decorative paper, and an optional overlay. This step starts by stacking a polypropylene sheet at the bottom, followed by three sheets of kraft paper (to make a thickness of around 2-3mm), one sheet of the selected decorative sheet, and one sheet of overlay (Fig. 3.5). The finishing plate is finally placed on top.

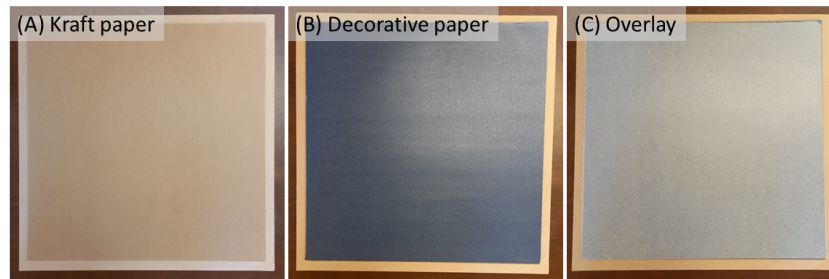


FIGURE 3.5: Stacking of a HPL: (A) kraft paper, (B) decorative paper and (C) overlay.

First, the press is pre-heated up to at least 145 °C. Once the press reaches the selected temperature, the doors open and the stack is placed inside the press to start the process. After the cooling steps end, and the press doors open, the laminate is cut and sanded and is characterized through the tests stated in the standard EN 438.

Three types of HPL were manufactured: (1) using a spray-coated overlay, (2) using only spray-coated decorative paper, and (3) using decorative paper impregnated with particles and exterior grade film, (EG film).

3.2.3 Manufacturing of Exterior grade High-pressure laminates

In this work, EUROPLEX® Film HC 0F701 was used. The film is applied on top of the HPL layers during the production process, without requiring additional adhesives and process steps. During the production, the bonding agent present in the PMMA-based film undergoes a chemical bonding process with the melamine resin-soaked decorative paper on the HPL panel, creating an inseparable covalent bond, which provides significantly improved adhesion and weather resistance compared to a physical bond. [13].

3.2.3.1 Synthesis of PMMA and spray deposition

Once the optimal particle and concentration were identified, to improve the homogeneity of the dispersion, the nanoparticles were dispersed in PMMA, to ensure both an improvement of the homogeneity of the dispersion and excellent bonding to the exterior

grade film (EUROPLEX® Film HC 0F701) applied over it. Acetone was selected as a solvent since it is chemically compatible with PMMA, is relatively low in toxicity, and has a fast evaporation rate, which means it quickly evaporates from the surface, leaving behind a clean and dry substrate [75].

PMMA purchased from Sigma Aldrich (6.64 g) was added to acetone (100 mL), 8.5 wt%, under magnetic stirring between room temperature and 40 °C for 1 hour until fully dissolved. Subsequently, 5 wt% of SiO₂ 60-70 nm particles (0.332 g) were added to the previous solution and magnetically stirred for 1 hour to obtain a uniform and transparent dispersion.

The dispersion was deposited on the 25.5×25.5 cm² decorative paper using a spray gun (Fig. 3.6). The diameter of the nozzle is 1.5 mm, and during spraying the distance between the spray gun was kept at the same distance as in the spray system (28 cm). The decorative papers sprayed with the PMMA/SiO₂ dispersion were used to manufacture HPL with EUROPLEX® Film HC 0F701.

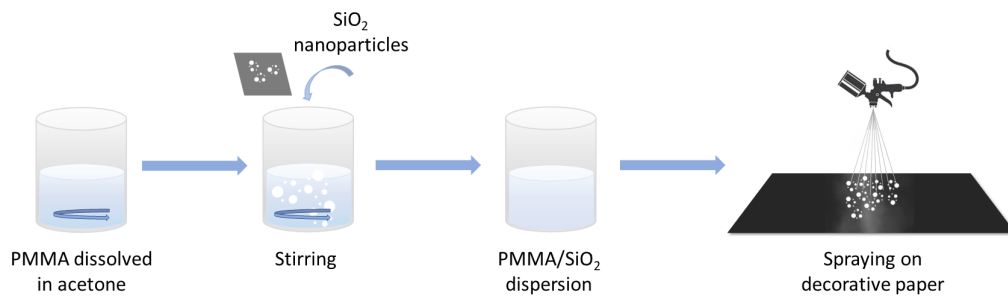


FIGURE 3.6: Preparation process for the PMMA/SiO₂ coating and deposition on the decorative paper.

3.3 Characterization techniques

3.3.1 Reflectance measurement

To evaluate the optical properties of a surface, it is fundamental to measure the reflectance over the entire solar spectral range. The spectral reflectance measurements in the ultraviolet (R_{UV} , 200 – 400 nm), visible (R_{VIS} , 400 – 700 nm), and near-infrared radiation (R_{NIR} , 700 – 1650) spectrum were determined and calculated according to the Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Sphere – ASTM E903 [76].

The experimental setup (Fig. 3.7) is comprised of a spectrophotometer, a light source, and a computer to perform and save the measurements. Two spectrophotometers coupled with different wavelengths, FLAME-T (UV-VIS) and FLAME-NIR (NIR), from Ocean Optics, were used to measure the reflectance of the samples in the 200-1650 nm region. The spectrometers combine the light from the light source, composed by two lamps, one of deuterium and the other of halogen. To measure directly on the sample, an integrating sphere (30 mm diameter) coupled to the spectrophotometer through fibre-optic cables (4.5 mm fiber diameter port) is required, which collects both specular and diffuse reflectance integrated over 360°, according to ASTM E903-96. The light source is connected to the sphere through a fibre-optic cable to apply the beam to the sample. The spectrophotometer is connected to a computer with a USB cable and a specific software reads the reflected light beam.

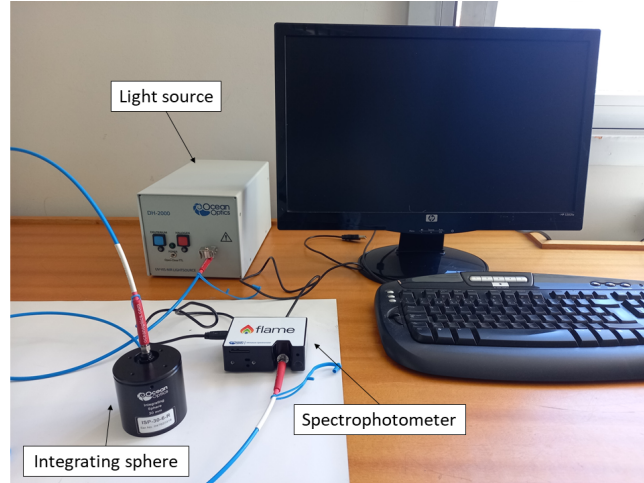


FIGURE 3.7: Reflectance measurement setup comprised of a spectrophotometer, an integrating sphere, a light source, and a computer to perform and save the measurements.

A Spectralon® disc (white standard) was used for the collection of the baseline, in interval measurements of 5 nm, considering that the absolute accuracy should be less than 0.02 units or approximately 2%.

The reflectance of each sample was averaged from 6 measurements at different points. The spectral reflectance values of the samples in the ultraviolet, visible, and wave near-infrared spectrum was calculated for the wavelengths listed on Table X2.1 100 ordinates Direct Normal Irradiance A.M. 1.5 of ASTM G173 [15] and following the procedure established in ASTM E903 [76]. The total reflectance ρ_s is obtained through

$$\rho_s = \frac{1}{n} \sum_{i=1}^n \rho(\lambda_i) \quad (3.1)$$

with n referring to the total number of wavelengths, $\rho(\lambda_i)$ being the corresponding reflectance for the wavelength λ_i .

3.3.2 Colour characterization

The final product has aesthetic value and, in order to evaluate any changes in the visual aspect of the laminates, the colour of the samples was assessed. Colourimetric measurements were taken with the same equipment for the reflectance measurement, as the FLAME-T spectrophotometer is suitable for colour evaluation using the CIE colourimetric coordinates.

The CIE colourimetric coordinates, lightness L^* (black–white), a^* (green–red) and b^* (blue–yellow), were used as recommended by the Commission Internationale de l’Eclairage (CIE). The procedure is similar to the one for reflectance measurements in the VIS spectrum. Starting by selecting the colour measurement in the menu of the software, to take the colour measurements in the CIELab colour space, the parameters for the conditions standard illuminant D65 and 10° observer were selected to simulate solar radiation.

The colour difference (ΔE) between two samples (sample 1 and 2) is calculated through equation 2.7.

3.3.3 Thermal behaviour evaluation

The thermal performance of the solar reflective HPL was investigated through the setup in Figure 3.8, similarly to that reported in the literature [14, 77, 78]. The setup consists of two IR lamps (Paulmann Incandescent lamp Infrared E27 230V 64lm 100W 1500K Red), two test XPS boxes and two PicoLog temperature data loggers.

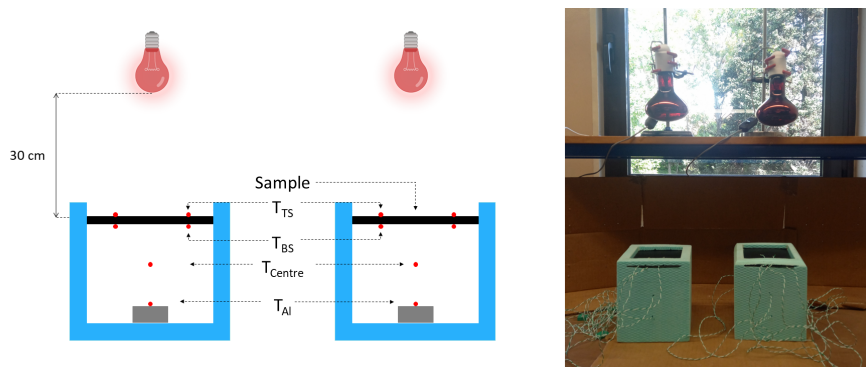


FIGURE 3.8: Schematic diagram and thermal behaviour measurement setup.

To study the relative cooling effect of an HPL doped with NIR reflective materials, two samples with size $14 \times 10 \times 0.8 \text{ mm}^3$ were inserted through an opening on the boxes, simulating the closed environment inside a room. Each sample was exposed to an IR lamp placed 30 cm above the sample. On each test set, the temperature was recorded by six k-type thermocouples glued with GE varnish to an aluminium block at the bottom of the box (T_{Al}), one placed at the centre position of the chamber (T_{Centre}), two glued to the bottom surface (BS) of the sample (T_{BS}), and two glued to the top surface (TS) of the sample (T_{TS}). Another thermocouple was placed outside to record the room temperature during the measurements. Even though the lamp irradiation does not correspond to the solar spectrum, considering the intention to evaluate the thermal behaviour of a coating containing NIR pigments, the lamps were chosen as they simulate a portion of the IR spectrum. The thermocouples were connected to two PicoLog temperature data loggers that recorded and collected the temperature data every 1 minute. The standard HPL sample was taken as the reference.

Two distinct tests were performed. The first test was implemented to assess the reproducibility of the experiment, evaluating if two different boxes yield concordant results with the use of the same reference sample. In the second test, the performance of EG and PMMA/ SiO₂ 5 wt% compared to a conventional HPL was evaluated.

Prior to taking the measurements, the thermocouples were allowed to equilibrate and stabilize at ambient temperature for 5 minutes. Afterwards, the IR lamps were turned on for 2 hours and 30 minutes. Lastly, the lamps were switched off and the sample was naturally cooled down.

3.3.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is one of the most versatile and highly effective instruments with the ability to image materials and structures with submicron resolution. SEM microscopes are designed primarily to examine material surfaces, allowing the observation and characterization of materials from a micrometre to a nanometer scale, providing information on the morphology, crystalline structure and chemical composition of materials. It is typically employed for the quantitative analysis of surface topography, from the measurement of the size of microstructures and their distribution/density, to quantifying the 3D morphology of objects, measuring particles (size and shape), and examining porosity and cracks.

A focused electron beam is used to focus the area to be analyzed, and can either be scanned across the surface to acquire information and form an image or be used static over a small area to obtain detailed information. As the beam reaches the specimen, it interacts with the specimen's surface, with the emission of X-rays, backscattered electrons (BE) and secondary electrons (SE). Backscattered electrons result from high energy incident electrons that are elastically scattered through an angle greater than 90 and provide a favourable signal for imaging the specimen and analysing its chemical composition. The secondary electrons are low-energy electrons that result from inelastic interactions between the electron beam and atoms at the sample surface, emitting loosely bound electrons, and are used for the production of high-resolution topographic contrast images with details of around 1–5 nm [79, 80].

A schematic diagram of the structure of a conventional SEM is depicted in Figure 3.9. A typical SEM layout comprises an electron gun, electromagnetic lenses to guide and focus the path of the electrons, a vacuum chamber containing a stage for the specimen and signal detectors.

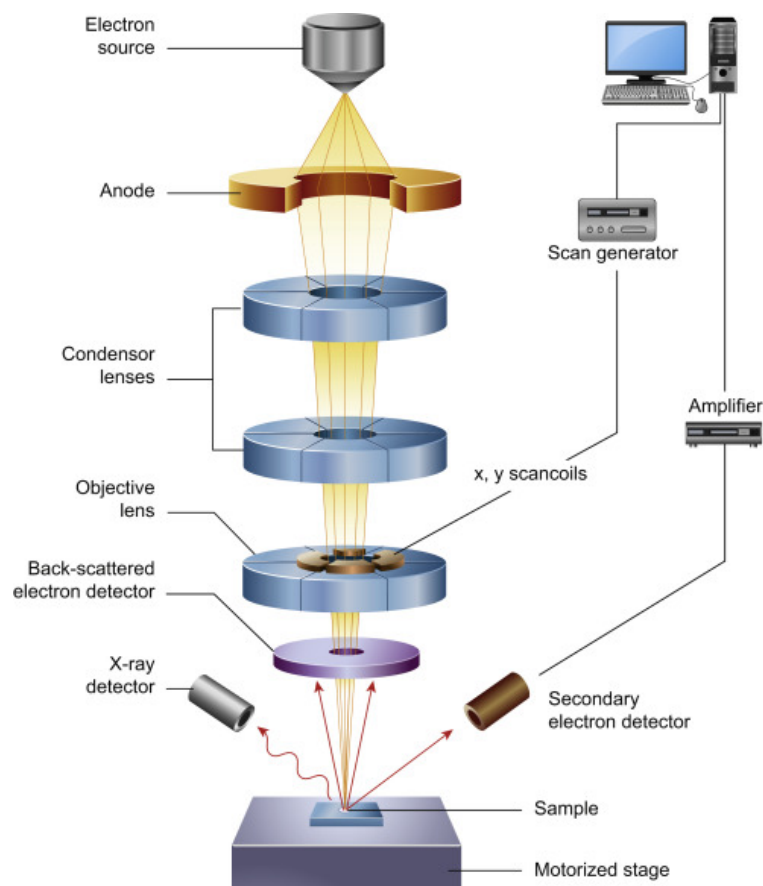


FIGURE 3.9: Schematic diagram of the core components of an SEM microscope. From ref. [80].

The electron gun, located at the top of the column, generates and accelerates the electrons to energy levels of typically 0.1 to 30 keV. Electromagnetic lenses and apertures are used to focus and shape the electron beam and to define a small focused electron spot on the specimen. The SEM should be operated in a high vacuum setting to reduce electron scattering. The specimen stage, electron beam scanning coils, signal detection, and processing system provide real-time observation and image recording of the specimen surface [79]. The specimens are attached to flat metal disk holders using carbon tape.

In the present study, a Phillips-FEI/Quanta 400 FEG high-resolution scanning electron microscope, at the Materials Center from University of Porto (CEMUP), was used for the morphological characterization of the samples, using an acceleration voltage of 15.00 kV. Images with 250 $\times$, 1000 $\times$, 5000 $\times$ and 20 000 $\times$ magnification were taken.

3.3.5 Energy-dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique to identify and quantify elemental compositions of samples [81]. EDX is typically used combined with SEM, enabling an analysis of the chemical composition. In a regular SEM, when the atoms on the surface are excited by the electron beam, specific wavelengths of X-rays characteristic of the atomic structure of the elements are emitted. These X-ray emissions are analyzed by energy dispersive detectors (a solid-state device that discriminates among X-ray energies) [81]. As the electron beam reaches the sample, the interactions between the beam and the material may result in the emission of characteristic X-rays. The energy of the emitted X-rays depends on the material under examination since each element has its own characteristic X-ray emission spectrum, and can thus be directly related to the corresponding chemical elements present in the specimen [82]. In a quantitative analysis, the concentration of a specific element present in a sample is measured by the intensities of peaks. For qualitative analysis, as each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum, different X-ray peaks with specified positions in a spectrum are identified [83].

In this study, EDX was used coupled with an SEM at CEMUP.

3.3.6 Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is an effective technique for the determination of functional groups in a sample and is applied for the identification of organic, inorganic and polymeric materials [84]. Alterations in the characteristic pattern of absorption bands indicate a change in the material composition [85].

Part of the IR radiation is absorbed by the sample, while other parts are transmitted through it, and the resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Each material has a unique composition and different arrangement of atoms, so each molecular structure possesses a singular IR spectrum, with absorption peaks that correspond to the frequencies of vibrations between the bonds of the atoms making up the material, and the size of the peak being a direct indication of the amount of material present [86].

Considering that transition energies corresponding to changes in vibrational energy states for many functional groups are located in the mid-IR region ($4000\text{--}400\text{ cm}^{-1}$), the presence of an absorption band in this region can be used to determine whether specific functional groups exist within the molecule. The spectrum can be divided into four regions, as represented in Figure 3.10.

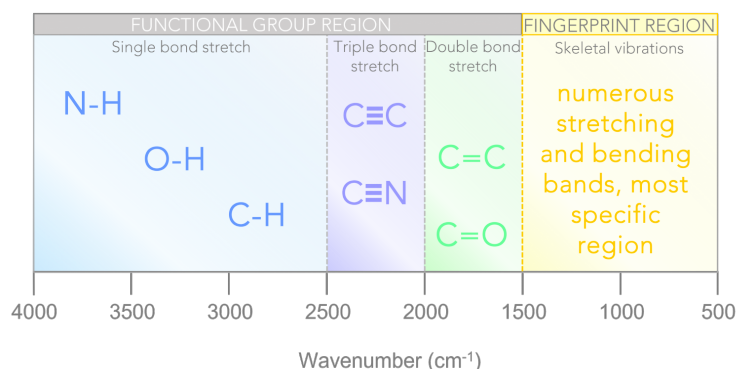


FIGURE 3.10: IR spectral regions. From ref. [87].

In this study, all FTIR spectra were acquired with a PerkinElmer Spectrum BX FTIR Spectrometer and a PIKE Technologies GladiATR (Fig. 3.11). In ATR-FTIR spectroscopy, an Internal Reflection Element (IRE) with a high refractive index is brought into contact with a sample with a lower refractive index. Total internal reflection occurs when the IR beam is directed at an angle above the critical angle. At the reflecting surface, an evanescent wave is generated, which then interacts with the sample, attenuating the infrared

light beam exiting the IRE. The detector receives the attenuated IR beam and converts the resulting signal into an IR spectrum [88] [89].



FIGURE 3.11: PerkinElmer Spectrum BX FTIR Spectrometer and a PIKE Technologies GladiATR.

3.4 Laminates characterization according to EN 438

To guarantee that the final product is in line with the client's needs, rigid quality control of both raw materials and the final product is required. This chapter presents the experimental procedures implemented to characterize the laminates, according to the norm EN-438 [6]. The following characterization tests were executed in the laboratory at Surforma.

3.4.1 Resistance to immersion in boiling water

This test starts by, for each of the three 50 mm × 50 mm specimens, measuring their mass and thickness at four different points. Hereafter, the specimens are fully submerged in boiling water for two hours (Fig.3.12).

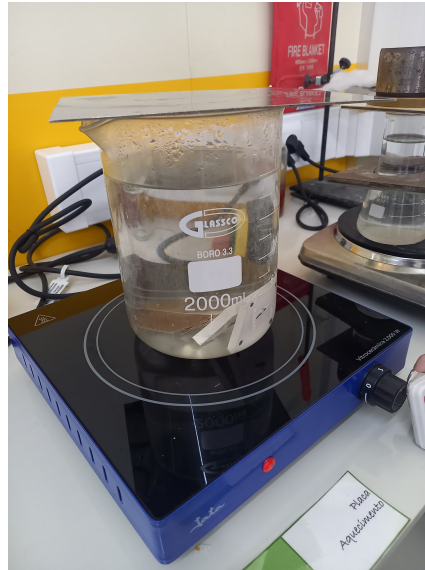


FIGURE 3.12: Resistance to boiling water equipment.

The specimens are removed and left to cool in running water for 15 min, followed by the measurement of their mass and thickness at the previously set points. Lastly, the superficial aspect is evaluated according to the scale presented in Table 3.1, requiring a minimal classification of 4. This test evaluates changes in mass and thickness of the samples, as well as alterations in the surface appearance when subjected to extreme conditions of temperature and humidity.

Rating	Description
1	Bubbles and/or delamination
2	Pronounced change in brightness and/or colour
3	Moderate change in brightness and/or colour
4	Minimal change in brightness and/or colour, only visible from certain angles
5	No visible changes

TABLE 3.1: Evaluation scale.

3.4.2 Resistance to water vapour

The resistance to water vapour test consists in placing the decorative side of the specimens, sized 100 mm × 100 mm, on top of Erlenmeyer flasks filled with boiling water (Fig. 3.13).



FIGURE 3.13: Water vapour test equipment.

For one hour, the specimens will be in contact with water vapour, after which they are removed and cleaned with absorbent paper, and left to rest for 24 hours. At last, the resulting superficial aspect is evaluated and classified from level 1 to 5, also in accordance with Table 3.1.

3.4.3 Resistance to scratching

The resistance to scratching of a laminate sheet is expressed as a numerical rating which defines the maximum applied load which does not produce a continuous surface scratch. The test result is verified by visually confirming that the next higher load step produces a continuous scratch. Two $100 \times 100 \text{ mm}^2$ specimens are placed in the risk apparatus (Fig. 3.14), and the test starts by making two scratches at 1.0 N load with a spacing of 1 to 2 mm between the marks. This procedure is repeated with increasing loads (2.0 N, 4.0 N, and 6.0 N), leaving enough space between each pair of scratches, until continuous scratch marks are evident. At last, the specimen is inspected in a lightbox to ascertain the rating according to Table 3.2, requiring a minimal classification between 1 and 3 according to the laminate grade.



FIGURE 3.14: Resistance to scratching test apparatus.

Rating scale	Discontinuous scratches, or faint superficial marks, or no visible marks	$\geq 90\%$ continuous double circle of scratch marks clearly visible
5	6 N	> 6 N
4	4 N	6 N
3	2 N	4 N
2	1 N	2 N
1	-	1 N

TABLE 3.2: Scratch resistance evaluation scale.

3.4.4 Resistance to abrasion

The abrasion resistance test evaluates the capability of a surface to endure abrasive wear, being performed to determine the initial point of wear (IP, corresponding to the first point in which to the point when the kraft paper gets exposed. For this test, two circular 120x120 mm² specimens and the abrasive paper strips are placed in the apparatus (Fig. 3.15).



FIGURE 3.15: Resistance to abrasion test apparatus.

Once the suction device and the number of revolutions are set, the abrading of the specimen can start. The abrasive paper strips have to be replaced after 500 revolutions. This test requires a close examination of the specimen's surface, and the final wear point (FP) corresponds to the point at which 95% of the kraft paper is exposed.

Using the determined IP and FP, the resistance to abrasion for each specimen is calculated using:

$$\text{Abrasion Resistance} = \frac{IP - FP}{2} \quad (3.2)$$

Chapter 4

High pressure laminates with the incorporation of NIR reflective particles

Overview

The incorporation of SiO₂ 1 μ m, SiO₂ 60-70 nm and TiO₂ 50 nm particles in the HPL's outer layer of HPL for improved solar reflectance was studied, and compared to a reference sample (a standard HPL without the addition of particles). Particle concentrations ranging from 1 wt% to 5 wt% were evaluated, as it is fundamental that the added particles do not induce colour alterations of the final HPL.

4.1 Incorporation of NIR reflective particles in the overlay of the HPL

4.1.1 Uniformity throughout the spray deposition line

During the deposition, it was noticeable that the coating was not uniform throughout the substrate, due to some spray guns releasing more dispersion than others. Additionally, this excess liquid drips, owing to the movement of the drier, leaving an intense line in the deposition direction. Therefore, to evaluate the uniformity of the coating deposited by the spray deposition line, reflectance and colour measurements were taken along the lines and columns of the substrate. The samples analysed are represented in Figure [4.1](#).

To simplify the quantity of specimens to analyse, it was decided to focus on only one line and column of the full substrate. A colour map highlighting the reflectance values obtained throughout the substrate is depicted in Figure 4.2. Warmer hues denote higher reflectance values and cooler hues signify lower values.

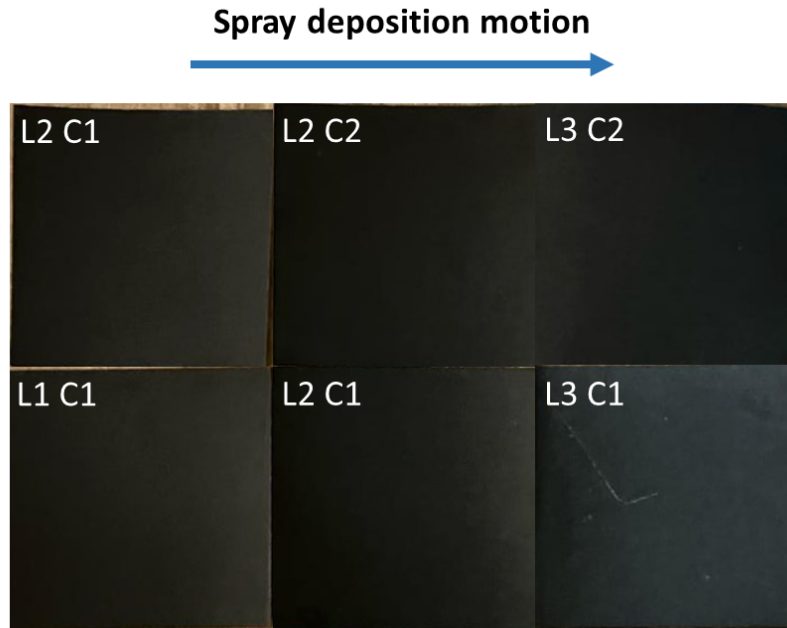


FIGURE 4.1: Analysed samples from the substrate by the direction of the spray motion.

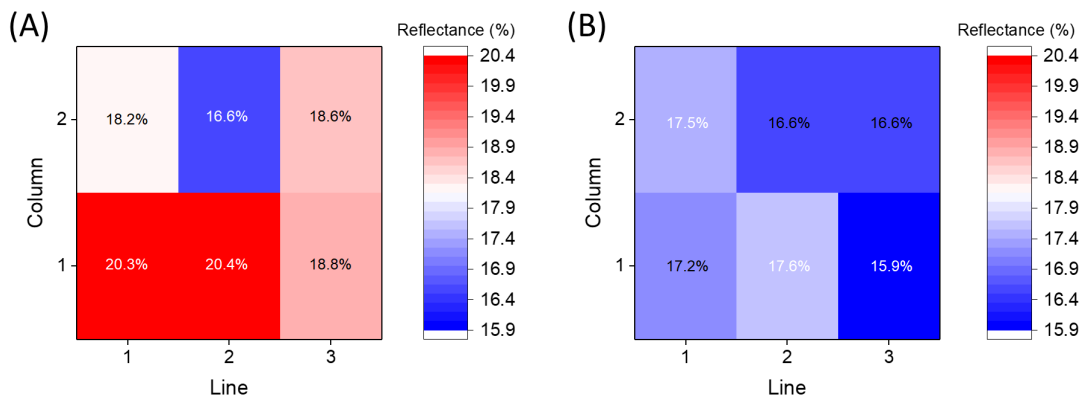


FIGURE 4.2: (A) Total and (B) NIR reflectance values through different areas of the substrate.

Through column 1, the reflectance reaches a maximum at line 2 (Fig. 4.3A). The sample with a higher reflectance value also presents higher colour differences (Fig. 4.3B). At line 3, the total and NIR reflectance are higher for the second column (Fig. 4.3C). As for the

colour differences, higher values of ΔE are obtained for the sample with higher total and VIS reflectance (Fig. 4.3D).

By line, perpendicularly to the spray deposition direction, the disparity between reflectance values for distinct columns is attributed to the different spray guns releasing different dispersion quantities. In the spray deposition direction, by column, inconsistencies in the reflectance values can be due to of the excess liquid that flows from the end of the line. Thus, in the following sections, to guarantee the uniformity of the study, the same areas of the substrate were selected for the sample's manufacturing.

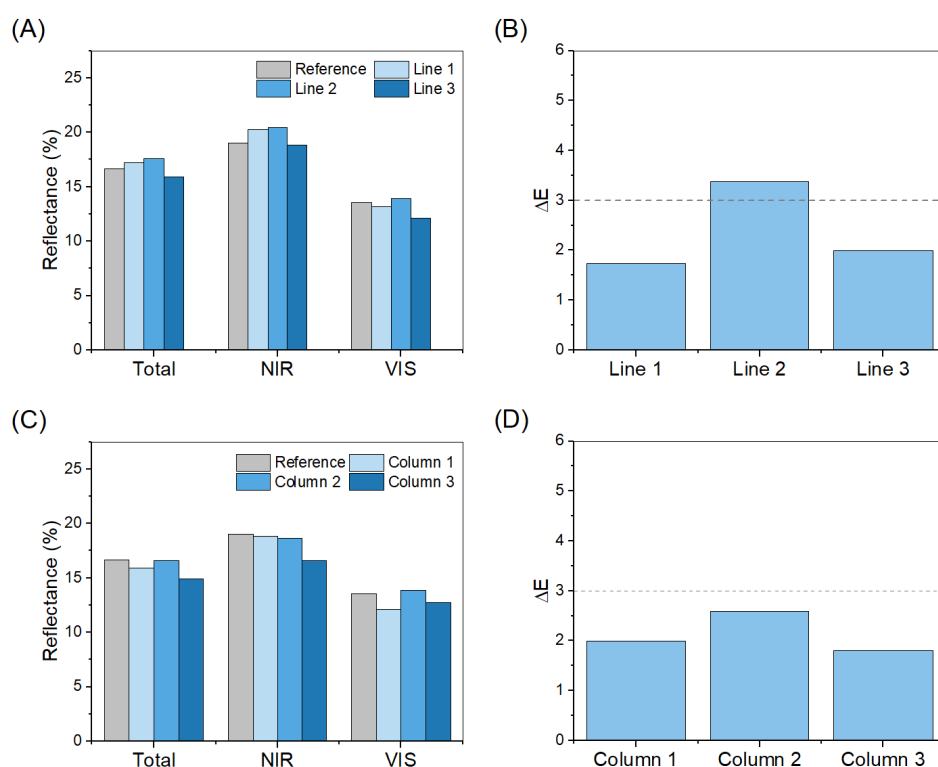


FIGURE 4.3: Study of the uniformity of the (A) reflectance and (B) colour by line, and (C) reflectance and (D) colour by column.

4.1.2 Incorporation of NIR reflective particles in the overlay of the HPL

For each particle under study, Figure 4.4 depicts the doped samples exhibiting the highest values of reflectance. Visually, the sample with SiO_2 nanoparticles appears the same as the reference sample. On the other hand, the samples with SiO_2 microparticles and the one with TiO_2 nanoparticles show some alterations compared to the reference.

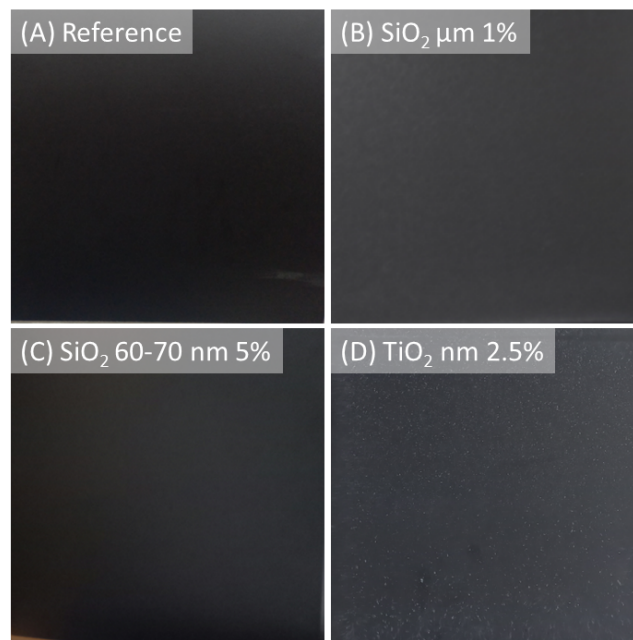


FIGURE 4.4: Samples with the deposition of (A) 1 wt% of SiO₂ 1 μm particles, (B) 5 wt% SiO₂ 60-70 nm particles and (C) 2.5 wt% TiO₂ 50 nm particles.

Figure 4.5 illustrates the spectral reflectance of the samples doped with SiO₂ 1 μm, SiO₂ 60-70 nm and TiO₂ 50 nm particles. With SiO₂ microparticles, the reflectance of the 1 wt% sample is the highest on both the VIS and NIR spectrums. In the SiO₂ nanoparticles case, the 1 wt% sample exhibits higher reflectance in the VIS spectrum. In the NIR spectrum, even though the 2.5 wt% and 5 wt% show similar reflectance values, the reflectance of the 2.5 wt% in the VIS spectrum is much lower than the latter. The reflectance values of the samples incorporating TiO₂ particles are higher than the ones obtained using SiO₂. The 2.5 wt% and 3.75 wt% samples show similar reflectance values; still, the overall reflectance is higher for the former.

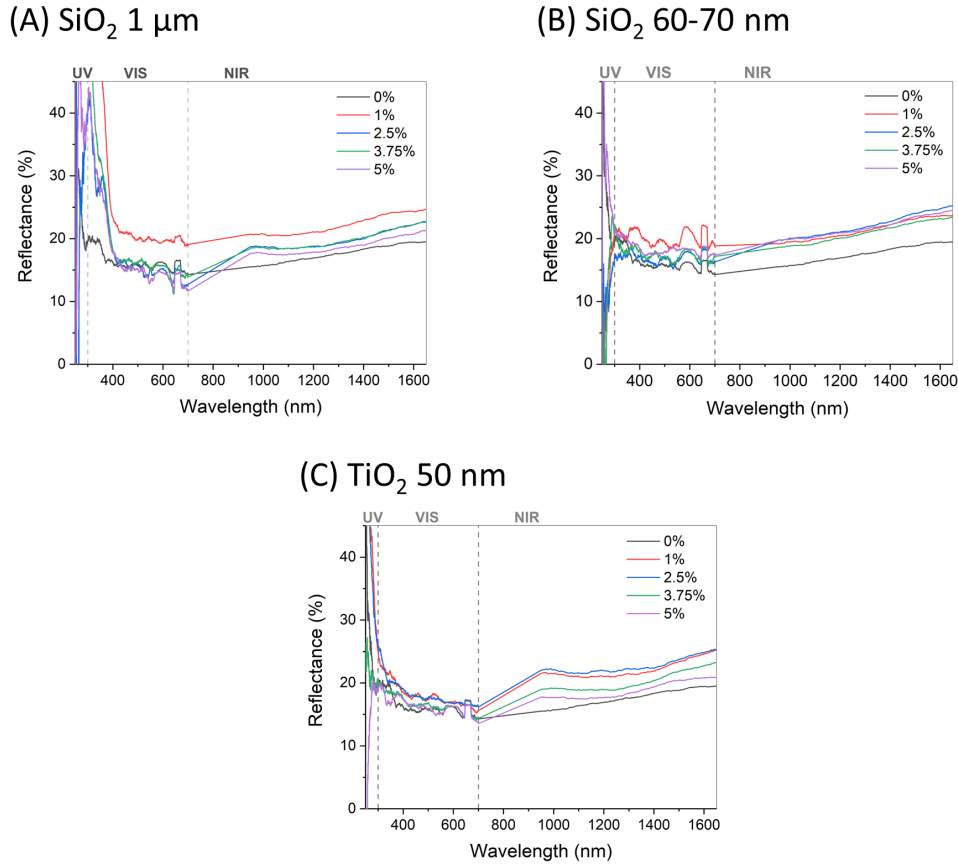


FIGURE 4.5: Spectral reflectance behaviour of the samples containing (A) SiO₂ 1 μ m, (B) SiO₂ 60-70 nm and (C) TiO₂ 50 nm.

The calculated total and NIR reflectance as a function of the weight concentration of the particles are displayed in Figure 4.6 and presented in Table 4.1 for the optimal cases. The incorporation of SiO₂ microparticles in the overlay (Fig. 4.6A) leads to a maximum in the total and NIR reflectances for a concentration of 1 wt%, with a relative increase of 25.3% and 21.2%, respectively, compared to the reference (16.5% and 16.2%).

Doping the overlay with SiO₂ nanoparticles (Fig. 4.6B), the maximum in NIR and total reflectance occurs for the 5 wt% sample, with a relative enhancement of 27.3% and 21.6% in comparison to the reference sample. Regarding these results, as the reflectance increases with the concentration of nanoparticles, one notes that a maximum of reflectance is yet to be reached.

The sample with a 2.5 wt% concentration of TiO₂ nanoparticles leads to a relative increase of 31.5% and 22.2% of the NIR and total reflectances, in comparison with the reference sample, as illustrated in Figure 4.6(C). With this type of particle, the reflectance

increases up to a 2.5 wt% concentration, with a decay of reflectance for larger concentrations.

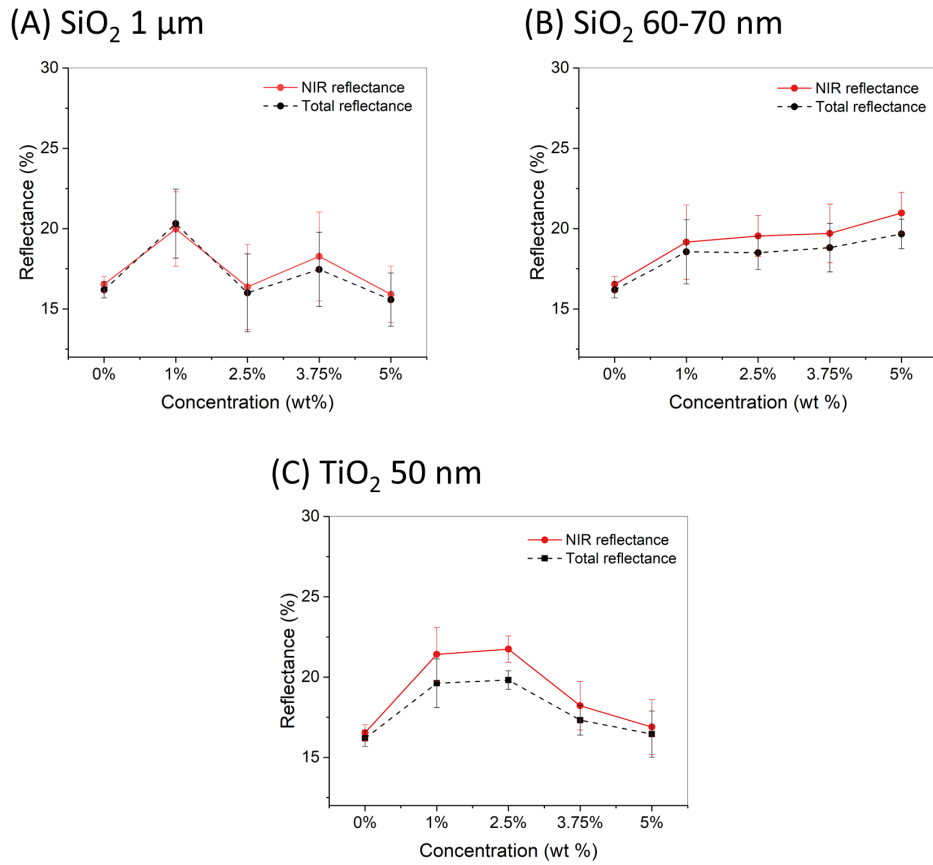


FIGURE 4.6: Calculated total average and NIR reflectance of the samples with the deposition of (A) SiO₂ 1 μ m particles, (B) SiO₂ 60-70 nm particles and (C) TiO₂ 50 nm particles.

Particle	Concentration (wt%)	R_{NIR}	R_{Total}	ΔR_{NIR}	ΔR_{Total}
-	Reference	16.5 %	16.2 %		
SiO ₂ 1 μ m	1.0 %	20.0 %	20.3 %	21.2%	25.3%
SiO ₂ 60-70 nm	5.0 %	21.0 %	19.7%	27.3%	21.6%
TiO ₂ 50 nm	2.5 %	21.7 %	19.8%	31.5%	22.2%

TABLE 4.1: Optimal NIR (R_{NIR}) and Total (R_{Total}) reflectance values obtained for each type of particle studied.

After the reflectance reaches a peak, a subsequent reduction is evident for concentrations beyond this threshold with both SiO₂ microparticles and TiO₂ nanoparticles, which can be due to the aggregation of the particles at large enough concentrations. In fact,

when two or more particles are closer together than the ideal spacing distance, they behave as a large aggregate resulting in a light scattering reduction [90]. Nanoparticles have a strong tendency to aggregate, so several surface-dispersing agents are commonly used to stabilize the particles in the coating formulation. However, the dispersing agents often lead to a loss of gloss or brightness and are incapable of maintaining a significant degree of spacing between the particles to enhance the light scattering [73, 90].

The overlap of scattering volumes of particles close to one another is intensified by increasing the concentration of the particles, resulting in the decrease of scattering efficiency [91]. In this situation, the scattering strength depends on the proximity of other particles, leading to the decrease of the scattering strength of individual pigment particles, for increasing concentrations [92, 93]. This phenomenon is known to occur in white paints pigmented with TiO_2 rutile particles, according to Auger et al. [91, 94]. For high particle concentrations, the distance between particles is lower, therefore there is an interaction between the light scattered by individual particles, ensuring a reduction of the scattering power [93]. Based on this understanding, the scattering coefficient is linearly related to concentration only for low concentrations (Beer's law region), while for higher concentrations, it falls below the linear value [93]. Accordingly, after a maximum in reflectance is reached, the decrease in reflectance for higher concentrations results from the increase in the number of particles, leading to a decrease in the total scattering, which can also be applied to the SiO_2 case.

To fully comprehend the behaviour of reflectance on the different spectrums, the calculated total, VIS and NIR reflectance are represented in Figure 4.7. Since black decorative paper is used throughout this study, the reflectance is expected to be lower than in other coloured surfaces. Nevertheless, the results clearly demonstrate that the deposition of nanoparticles in the outer layer increases the reflectance of the sample. This indicates that the introduction of NIR reflective particles in the HPL is promising for the improvement of its thermal performance.

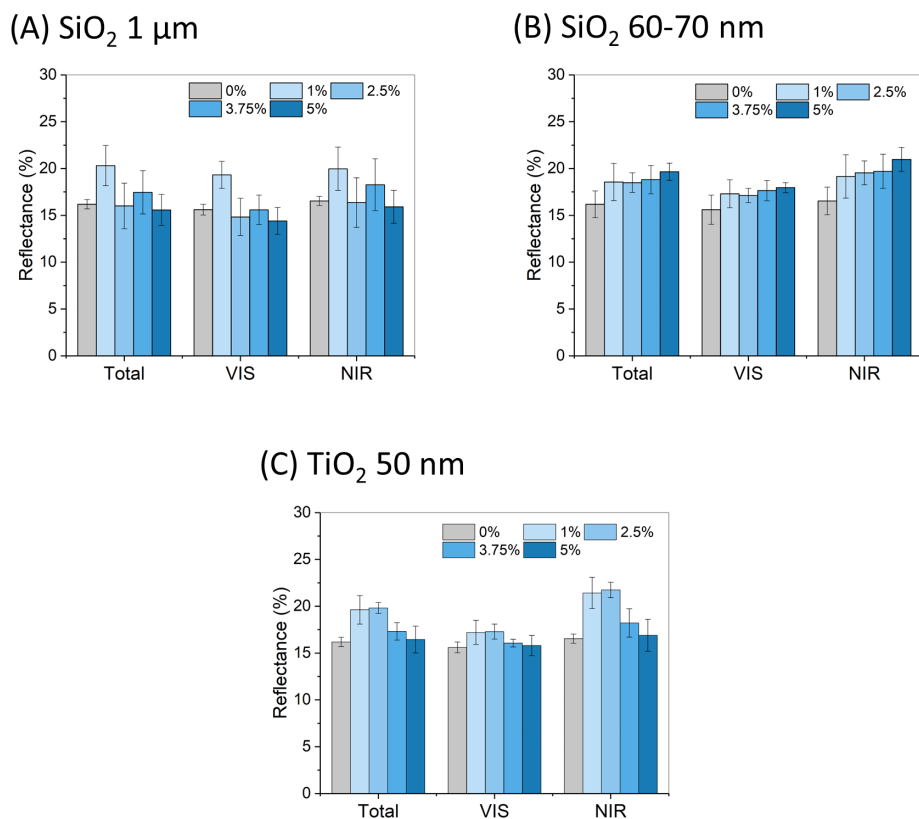


FIGURE 4.7: Calculated reflectance in the different spectrums of the samples with the deposition of (A) SiO₂ 1 μm particles, (B) SiO₂ 60-70 nm particles and (C) TiO₂ 50 nm particles.

The objective of this study is to improve the characteristics of HPL for exterior use without compromising its aesthetic qualities. Therefore, the colourimetric assessment is a crucial factor to consider when formulating dispersions containing the particles.

Regarding the samples containing SiO₂ microparticles, even though the 1 wt% sample displays the highest increase of reflectance, the colour alteration reported (Fig. 4.8A) is greater than the established threshold ($\Delta E \leq 3$). With both SiO₂ (Fig. 4.8B) and TiO₂ (Fig. 4.8C) nanoparticles, the samples with the highest reflectance show a ΔE below the threshold. Despite the deposition of TiO₂ nanoparticles being noticeable on all the samples, the ΔE obtained for the sample with the highest reflectance (3.75 wt%) is below the acceptable threshold.

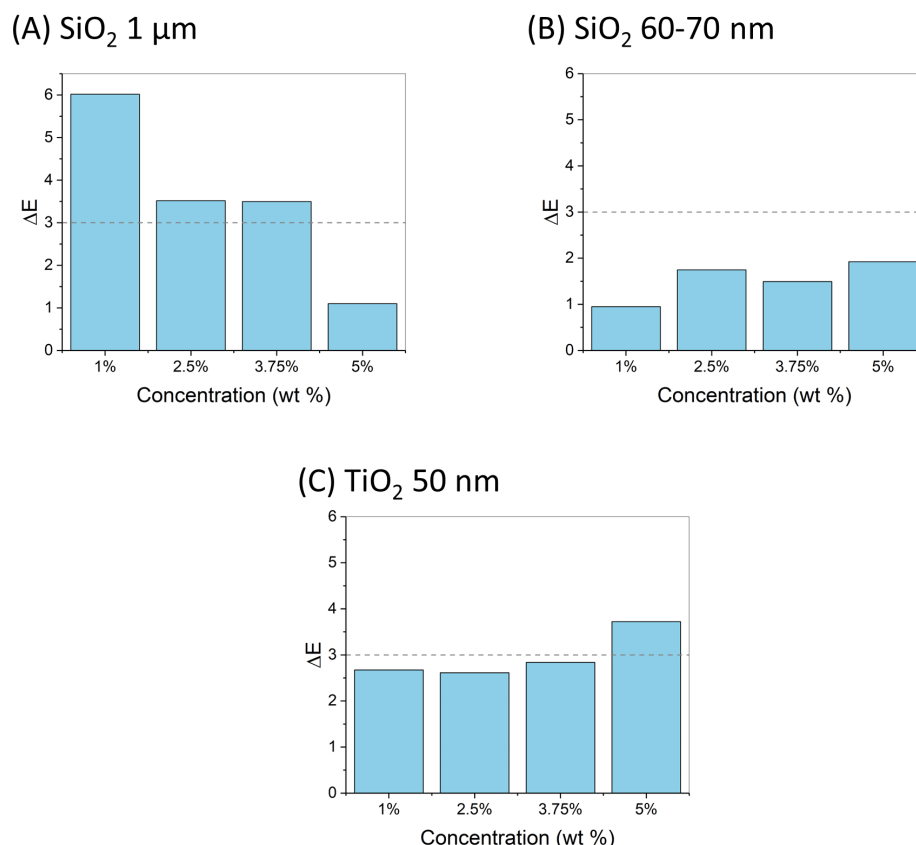


FIGURE 4.8: Calculated colour differences of the samples with the deposition of (A) SiO_2 1 μm particles, (B) SiO_2 60-70 nm particles and (C) TiO_2 50 nm particles.

SEM analysis was carried out to characterize the morphology of the samples with a 2.5 wt% concentration of SiO_2 1 μm , SiO_2 60-70 nm and TiO_2 50 nm. The obtained SEM images are presented in Figure 4.9. The images of the samples with added particles present a heterogeneous distribution of particles. SiO_2 1 μm particles are detected for the range of concentrations evaluated, and it is possible to notice mixed sizes and shapes. For the 2.5 wt% SiO_2 60-70 nm and TiO_2 50 nm samples, particle aggregation is observed and, on account of the particle size, it is not possible to spot individual particles in the polymer matrix (resin). The specimens analysed only comprise a small area of the sample, and their heterogeneous nature indicates that the deposition of the particles does not guarantee a uniform distribution. As a result, the examined specimen may not be a good representation of the whole sample. During the impregnation (on the pressing stage) there is a possibility that some particles can migrate deeper into the paper, and the SEM limitations in penetrating deeper within the sample prevents the proper assessment of the particles distribution.

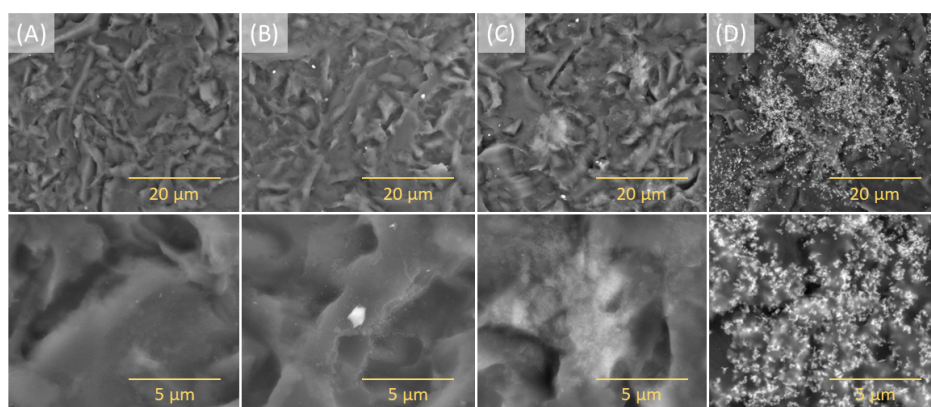


FIGURE 4.9: Scanning electron microscopy images of (A) reference, (B) SiO_2 1 μm , (C) SiO_2 60-70 nm particles and (D) TiO_2 50 nm particles. Magnifications: 5000 $\times$, 20 000 $\times$

Figure 4.10 displays the IR absorbance of the reference (black), SiO_2 1 μm 1% (red), SiO_2 60-70 nm 5% (blue) and TiO_2 50 nm 2.5% (green). In the relevant wavelength range between 8 and 13 μm , in the ATW, the FTIR spectrum of all samples shows significant absorption between 12.5 and 12.6 μm , 10.3 and 10.4 μm , and 8.6 and 8.9 μm . In the SiO_2 spectra, the appearance of peaks at 8.6-8.9 μm and 12.5-12.6 μm are attributed to the vibration absorption from Si–O–Si bonds [95, 96]. The peak around 8.6-8.9 μm in the TiO_2 is assigned to the bending vibrations of Ti–O groups. The absorption at 10.3-10.4 μm can be attributed to C–H bending vibrations from the melamine resin [97] in the overlay and decorative paper.

The absorption peaks are higher in both SiO_2 samples compared to the TiO_2 one, in view of the relevant Si-based functional groups in the ATW. At 12.5-12.6 μm the absorption is stronger in the SiO_2 nm specimen, as a result of the higher silica concentration. The significant absorption/emittance in the ATW demonstrated by both SiO_2 samples indicates a favourable contribution to releasing excess heat in this wavelength range, using the radiative cooling principles.

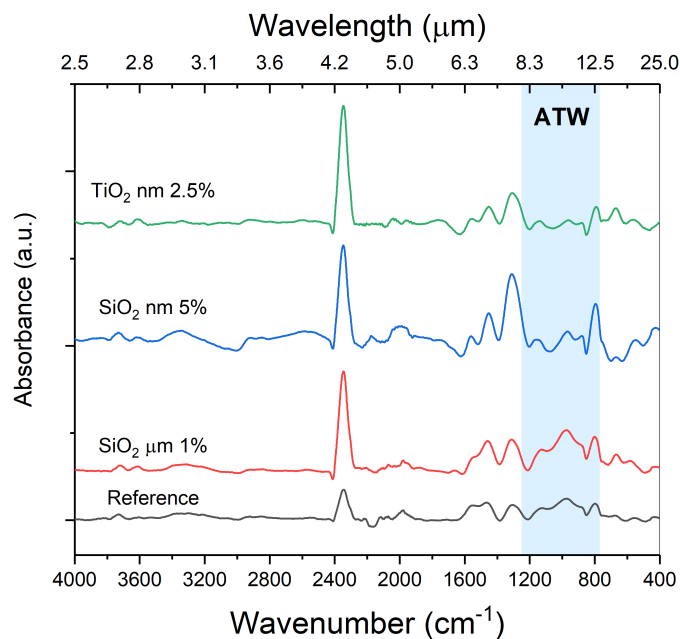


FIGURE 4.10: FTIR spectrum of reference (black), SiO₂ 1 μ m 1% (red), SiO₂ 60-70 nm 5% (blue) and TiO₂ 50 nm 2.5% (green).

4.2 Incorporation of NIR reflective particles in the decorative paper of the HPL

Since unicolour HPL does not require the use of overlay, the effect of SiO₂ 60-70 nm and TiO₂ 50 nm particles on the decorative paper as the outer layer was evaluated. SiO₂ 1 μ m particles were not applied in this study since their use led to the lowest NIR reflectance relative increase. Figure 4.11 shows the samples incorporating SiO₂ and TiO₂ nanoparticles that presented the highest reflectance values.

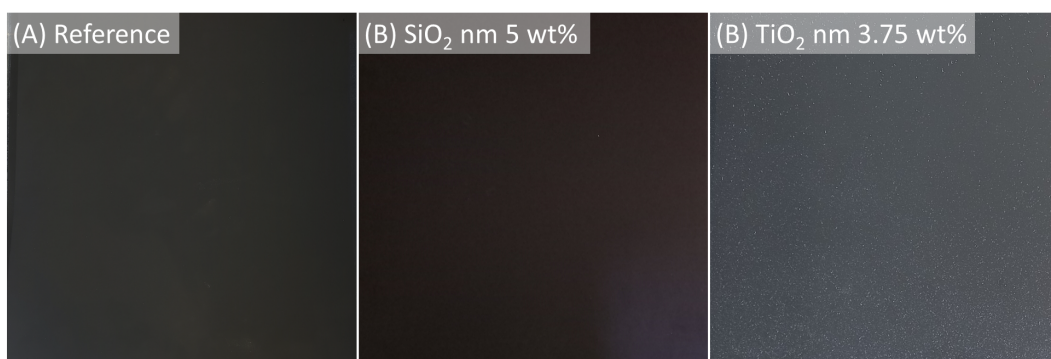


FIGURE 4.11: Samples with the deposition of (A) 5 wt% SiO₂ 60-70 nm particles and (B) 3.75 wt% TiO₂ 50 nm particles on the decorative paper.

The spectral reflectance of the SiO_2 and TiO_2 shows a similar behaviour as that seen previously. On the full range of the SiO_2 spectrum, the reflectance of the 10 wt% sample is the highest. As for the TiO_2 sample, in the VIS spectrum, the reflectance of all concentrations studied is higher than the reference, and the opposite behaviour is observed in the NIR spectrum. The reflectance of the samples with the particles deposited in the decorative paper is lower than the values obtained when the deposition of particles is performed in the overlay, taking into consideration that the former substrate exhibits a darker colour.

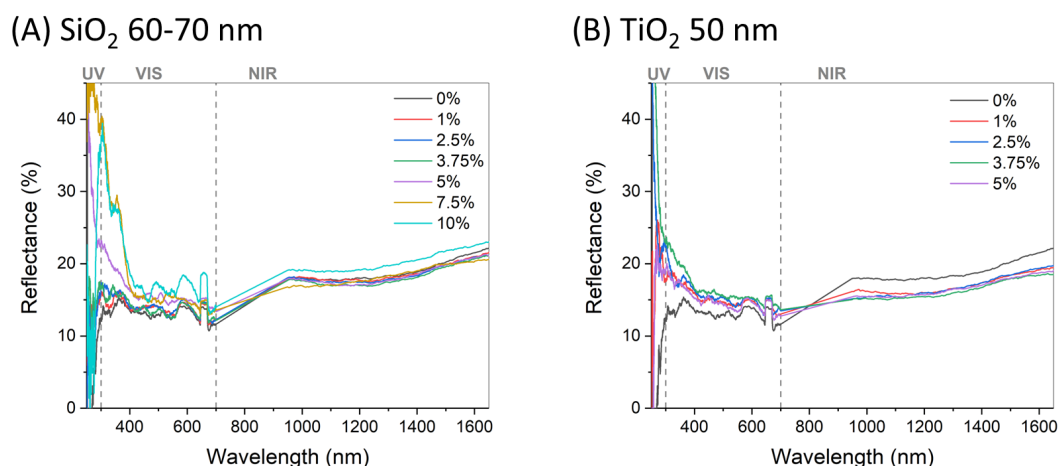


FIGURE 4.12: Spectral reflectance behaviour of the (A) reference sample and samples containing (B) SiO_2 60-70 nm and (C) TiO_2 50 nm.

Figure 4.13(A) shows the HPL reflectance as a function of the concentration of incorporated SiO_2 nanoparticles. As in the previous case, the reflectance increases with the particle concentration, and the 5 wt% sample presents the highest NIR and total reflectance (Table 4.2) with relative increases of 20.1% and 18.8%. With the use of TiO_2 nanoparticles, the reflectance increases to a maximum for a 3.75 wt% concentration (Fig. 4.13B). The highest values obtained for the NIR and total reflectance (Table 4.2) show relative improvements of 14.6% and 16.7% above the reference values, respectively.

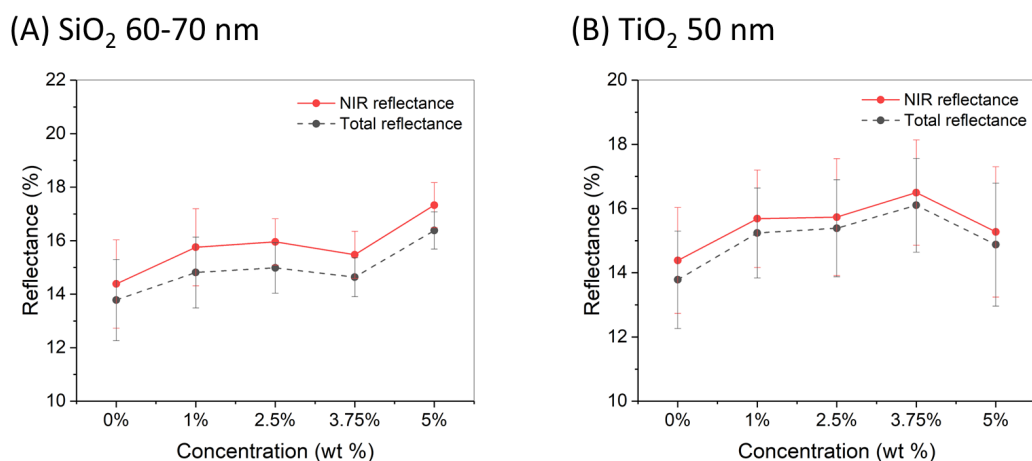


FIGURE 4.13: Calculated total average and NIR reflectance of the samples with the deposition of (A) SiO₂ 60-70 nm particles and (B) TiO₂ 50 nm particles.

Particle	Concentration (wt%)	R_{NIR}	R_{Total}	ΔR_{NIR}	ΔR_{Total}
-	Reference	14.4 %	13.8 %		
SiO ₂ 60-70 nm	5.0 %	17.3 %	16.4 %	20.1%	18.8%
TiO ₂ 50 nm	3.75 %	16.5 %	16.1 %	14.6%	16.7%

TABLE 4.2: Maximum NIR (R_{NIR}) and Total (R_{Total}) reflectance of the SiO₂ and TiO₂ doped HPLs.

The colour difference of the samples increases with the concentration of SiO₂ nanoparticles (Fig. 4.14A), and, as expected, increasing the concentration of nanoparticles added leads to increasing colour differences. Since ΔE is still below the threshold ($\Delta E < 3$), it is possible to further increase the concentration to determine the value that leads to the optimal reflectance. For the range of concentrations studied, the colour differences with the addition of TiO₂ nanoparticles are satisfactory (Figure 4.14B). However, the deposited particles are noticeable on the samples.

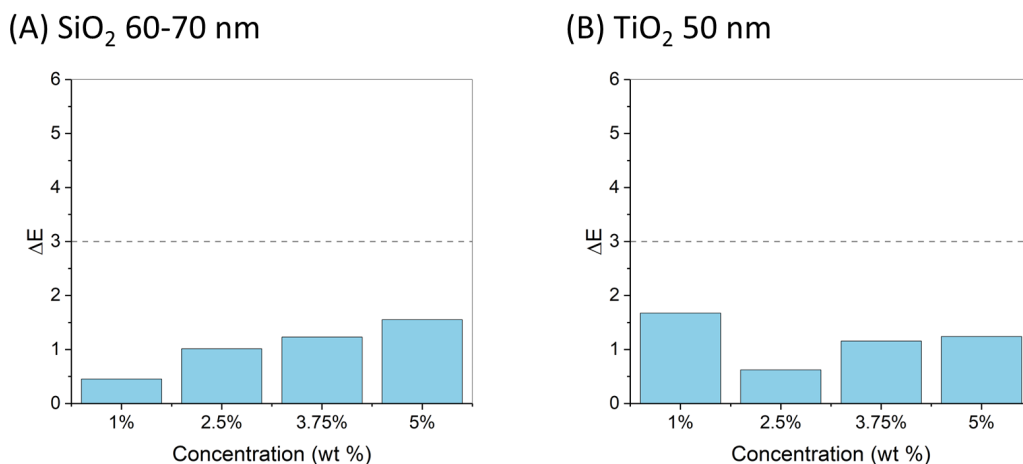


FIGURE 4.14: Calculated colour differences of the (A) SiO₂ 60-70 nm doped HPLs and (B) TiO₂ 50 nm doped HPLs.

To determine if increasing concentrations of SiO₂ nanoparticles lead to a higher reflectance improvement, additional concentrations of 7.5% and 10% were evaluated. The samples with 7.5 wt% and 10 wt% of SiO₂ are displayed in Figure 4.15.

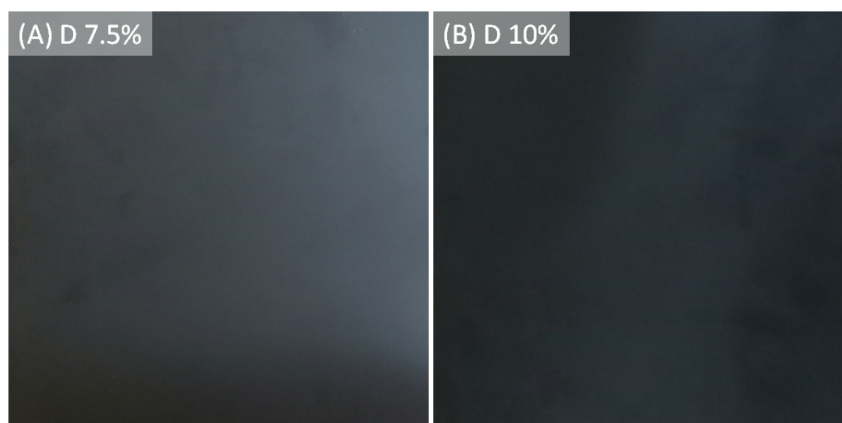


FIGURE 4.15: SiO₂ 60-70 nm doped HPL with (A) 7.5 wt% and (B) 10 wt% content.

The total and NIR reflectance and colour variations are represented in Figure 4.16. The NIR reflectance does not improve for higher concentrations, having reached the maximum for the 5 wt% concentration, while the total reflectance increases with the particle content. The colour alterations of the sample further increase with the concentration of nanoparticles, and the 10% sample has a ΔE greater than the threshold. Considering the reflectance and colour differences, the sample with a 5 wt% concentration of SiO₂ nanoparticles is the optimal one, compromising both Nir reflectance and colour.

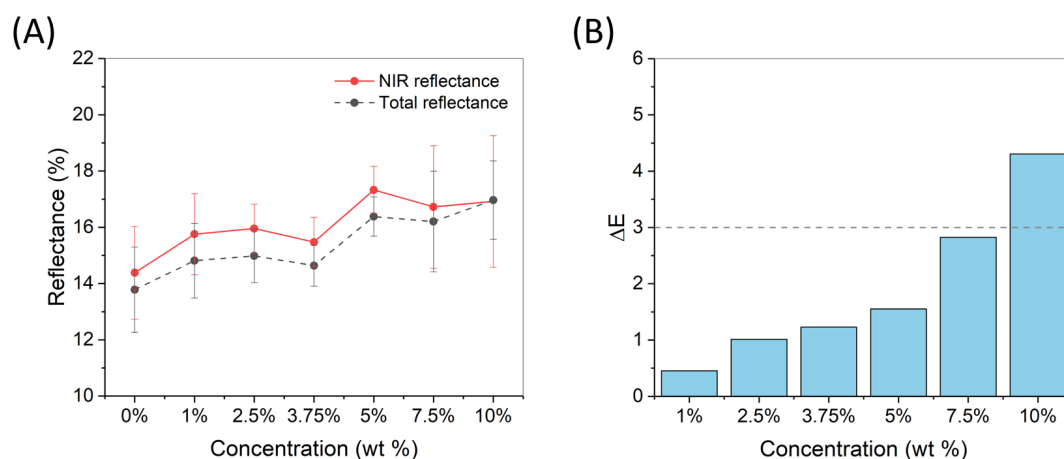


FIGURE 4.16: (A) Calculated total and NIR reflectance and (B) colour alterations of the samples with the deposition of SiO₂ 60-70 nm particles.

The SEM images obtained for the reference, SiO₂ 5 wt% and TiO₂ 3.75 wt% concentration samples are shown in Figure 4.17. A heterogeneous distribution and aggregation of particles is observed on the samples containing nanoparticles. Similarly to the previous case, there is a possibility that some of the nanoparticles are below the surface.

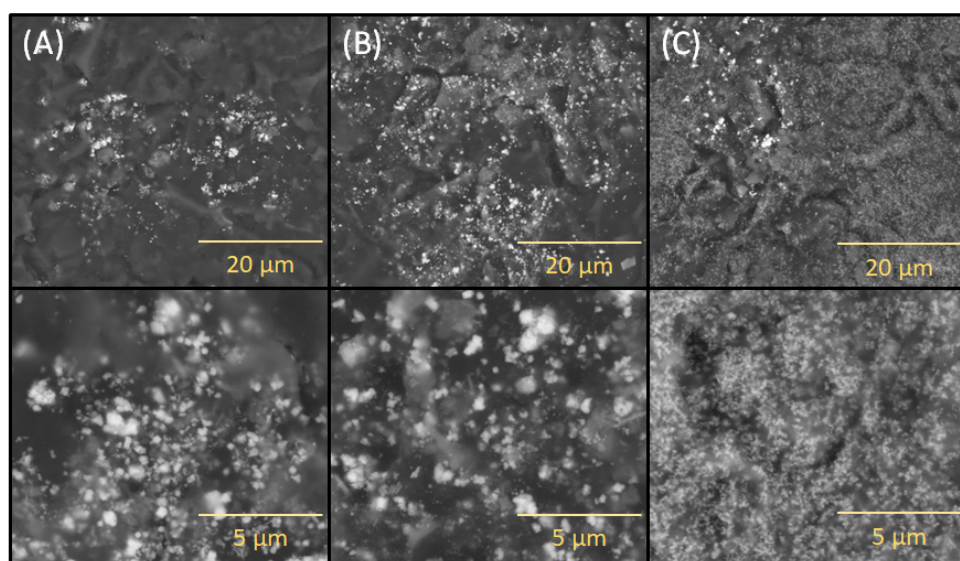


FIGURE 4.17: Scanning electron microscopy images of (A) reference, (B) SiO₂ 60-70 nm 5% and (C) TiO₂ 50 nm 3.75%. Magnifications: 5000 $\times$, 20 000 $\times$

Figure 4.18 shows the FTIR spectrum of the SiO₂ 60-70 nm 5% (black) and TiO₂ 50 nm 3.75% (red) samples. Significant absorbance peaks are observed in the ATW, at 8.7 μm for SiO₂ and TiO₂, 10 and 12.5 μm, and 10.3 and 12.4 μm for SiO₂ and TiO₂, respectively. All of the absorption peaks observed are assigned to the bonds described in section 4.1. The

absorbance/emittance of the SiO_2 sample is more evident than the results for the TiO_2 sample, suggesting a possible contribution to release energy by thermal radiation.

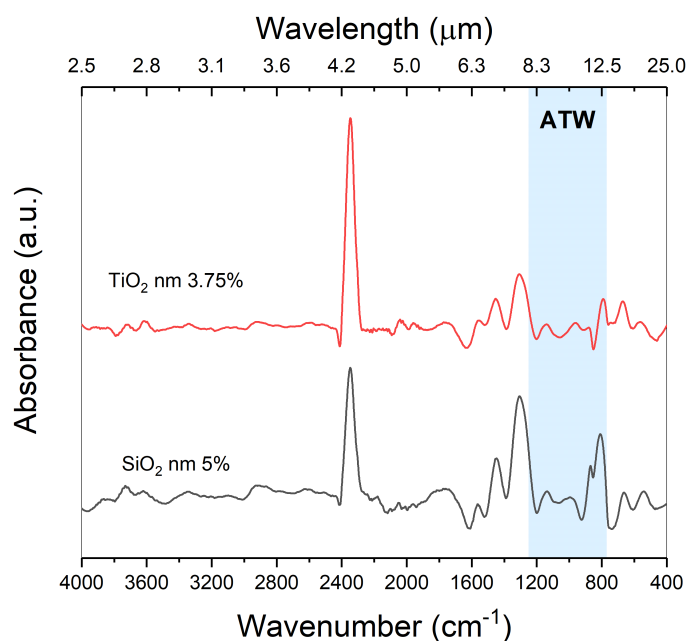


FIGURE 4.18: FTIR spectrum of SiO_2 60-70 nm 5% (black) and TiO_2 50 nm 3.75% (red).

4.3 Multilayer - Overlay and decorative paper with nanoparticles

The influence of both overlay and decorative paper containing nanoparticles on the improvement of the reflectance of HPLs was studied. For each nanoparticle, the overlay and decorative paper with the highest reflectance were chosen. Sample ST1 (Fig. 4.19A) is constituted by an overlay with SiO_2 5% and decorative paper with TiO_2 3.75%, while sample TS1 (Fig. 4.19b) is constituted by an overlay with TiO_2 2.5% and decorative paper with SiO_2 5% (Table 4.3).

Sample	Overlay	Decorative paper
ST1	SiO_2 5%	TiO_2 3.75%
TS1	TiO_2 2.5%	SiO_2 5%

TABLE 4.3: Overlay and decorative paper contitution of the multilayer samples.



FIGURE 4.19: ST1 and TS1 samples.

Figure 4.20 illustrates the spectral reflectance of the multilayer samples, ST1 (red) and TS1 (blue). The reflectance of both ST1 and TS1, in the full spectral range, exceeds the reference value.

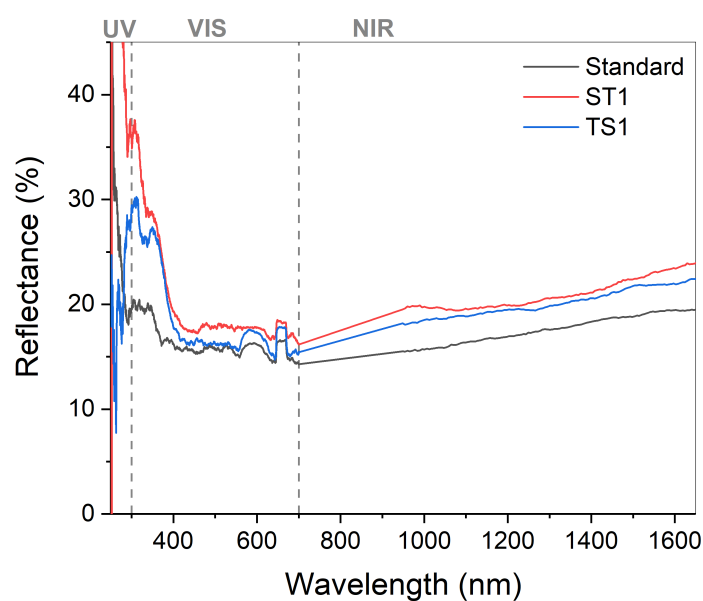


FIGURE 4.20: Spectral reflectance of the ST1 (red) and TS1 (blue) samples.

As illustrated in Figure 4.21, both ST1 and TS1 samples have reflectance values (Table 4.4 below the ones obtained with the single use of the overlay with the inclusion of nanoparticles. The NIR and total reflectance improvement of the ST1 sample is of 20.0% and 17.9% above the reference, respectively. The TS1 sample reports improvements of 7.3% and 7.4%, for the NIR and total reflectance. Thus, the combined application of both overlay and decorative paper impregnated with nanoparticles does not further increase

the reflectance of the samples. Finally, the colour variation of the ST1 and TS1 samples is lower than the established limit (Fig. 4.21B).

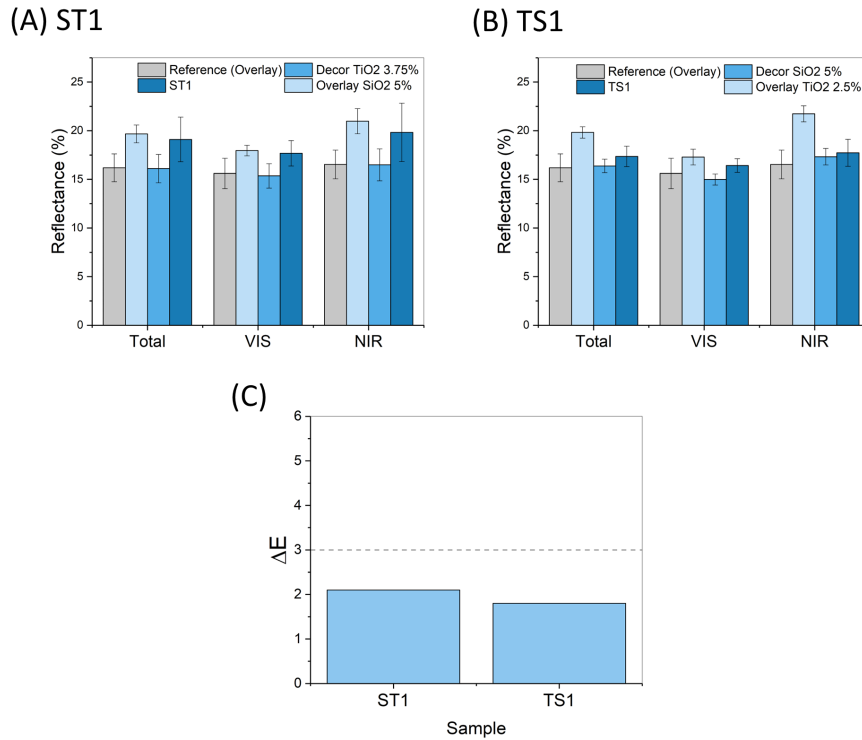


FIGURE 4.21: Calculated total average and NIR reflectance of the (A) ST1 and (B) TS1 samples; (C) Calculated colour alterations of the ST1 and TS1 samples.

Sample	R_{NIR}	R_{Total}	ΔR_{NIR}	ΔR_{Total}
ST1	19.8%	19.1%	20.0%	17.9%
TS1	17.71%	17.4%	7.3%	7.4%

TABLE 4.4: NIR (R_{NIR}) and Total (R_{Total}) reflectance of the ST1 and TS1 samples.

4.4 HPL using exterior grade films

Considering that the incorporation of SiO₂ nanoparticles in the decorative paper leads to the highest reflectance increases without excessive influencing the visual aesthetic of the HPL, these particles were selected to produce samples using an Exterior grade Europlex 0F701 film.

Figure 4.22 illustrates the FTIR spectra of the EG film (black), decorative paper (red) and overlay (blue). The spectrum obtained for the EG film shows a significant absorption peak at 8.7 μm , which can be derived from the CF₂ stretching vibration of PVDF or CH₂

bending of PMMA. This strong absorption peak is a favourable indicator that the emissivity of the EG film the ATW can contribute to a radiative cooling effect. Additional peaks at 10.3 and 12.1 μm are attributed to the CH_2 bond of PVDF. Both overlay and decorative paper are impregnated with melamine resin, and the absorption at 8.6-8.7 μm , 10.2-10.3 μm and 12.7 μm results from the NH_2 rocking, C-H bending and C-N bending vibration of the melamine resin, respectively [97].

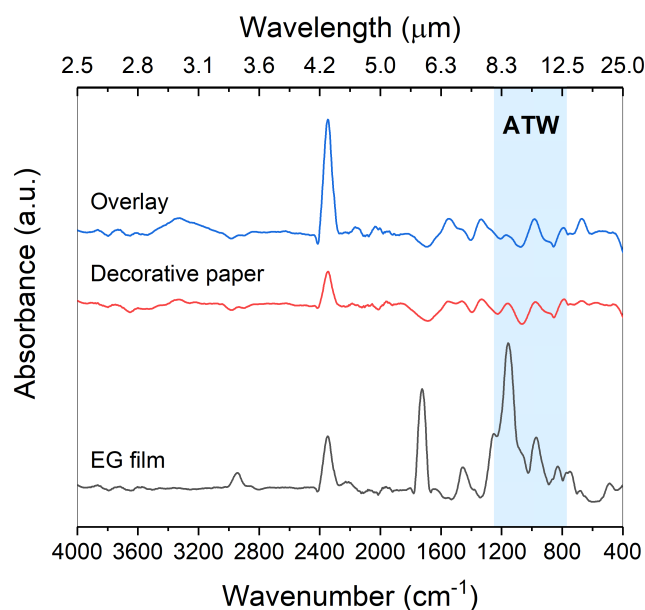


FIGURE 4.22: FTIR spectrum of the overlay (blue), decorative paper (red) and EG film (black).

4.4.1 Exterior grade film and decorative with nanoparticles

Figure 4.23 shows the samples produced using Exterior grade film and decorative paper doped with 5%, 7.5% and 10 wt% SiO_2 nanoparticles. Visually, the 5 wt% sample appears to show no differences when compared to the reference sample. The 7.5 wt% sample presents perceptible white dots, attributed to the heavier deposition of the dispersion, as seen previously. In the 10 wt% sample some dots from the deposition are visible from certain angles.

The spectral reflectance of the SiO_2 -doped EG HPL are illustrated in Figure 4.24. The three samples present an identical behaviour, with similar reflectance values on all spectra, showing a significant improvement relative to the standard EG HPL. These results demonstrate that the EG film could likely be influencing the reflectance of the doped samples.



FIGURE 4.23: Samples with (A) Exterior grade film and decorative paper with (B) 5 wt%, (C) 7.5 wt% and (D) 10 wt% SiO₂ nanoparticles concentration.

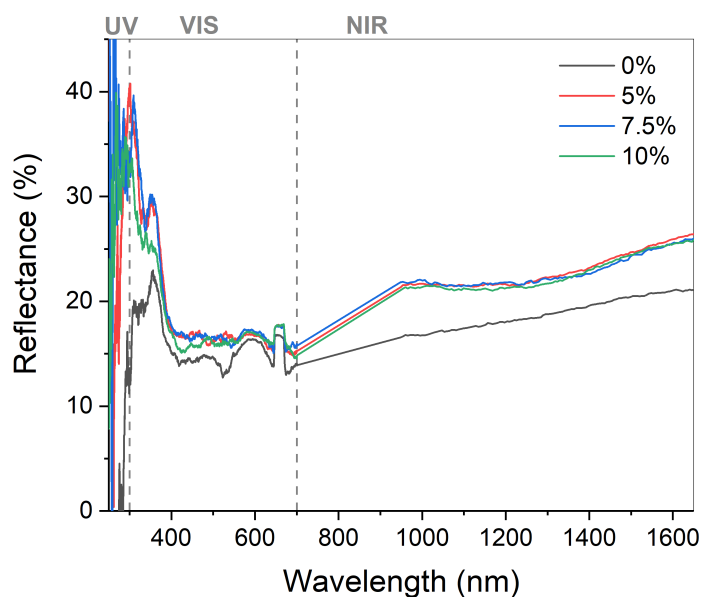


FIGURE 4.24: Spectral reflectance of the EG HPL with 5 wt% (red), 7.5 wt% (blue) and 10 wt% (green) SiO₂ nanoparticles.

The reflectance and colour differences (Table 4.5) of the samples constituted by the EG film and SiO₂-doped decorative paper are represented in Figure 4.25. Although the most significant increase in NIR and total reflectance (Table 4.5) is obtained for the sample

with 7.5 wt% (37.4% and 31.4% above the reference), this sample has significant colour alterations ($\Delta E = 4.1$). In fact, the 7.5 wt% sample (Fig. 4.23B) presents noticeable white dots, as a result of an unsatisfactory deposition, explaining the ΔE obtained. The 5 wt% sample displayed improvements in NIR and total reflectance of 31.6% and 23.5% above the reference values, maintaining acceptable colour differences ($\Delta E = 1.5$).

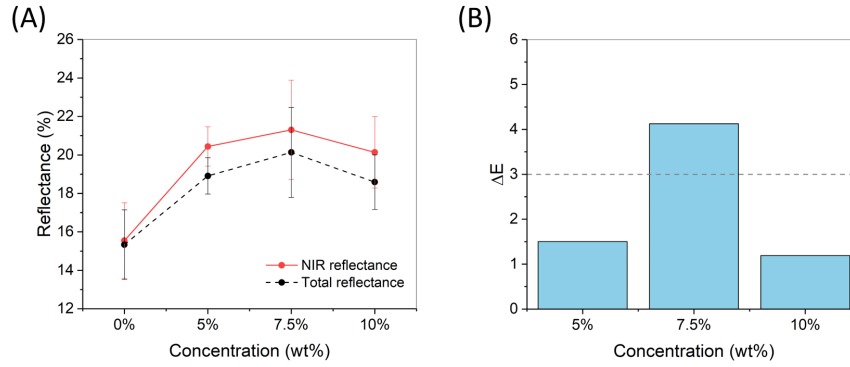


FIGURE 4.25: (A) Calculated total average and NIR reflectance and (B) colour differences of the EG samples

Concentration (wt%)	R_{NIR}	R_{Total}	ΔR_{NIR}	ΔR_{Total}
EG Reference	15.5 %	15.3 %		
5.0 %	20.4 %	20.1 %	31.6%	23.5%
7.5 %	21.3 %	20.1 %	37.4%	31.4%
10 %	20.1 %	18.6 %	29.7%	21.6%

TABLE 4.5: NIR (R_{NIR}) and total (R_{Total}) reflectance and relative reflectance increase (ΔR_{NIR} and ΔR_{Total}) values obtained for each SiO₂ 60-70 nm concentration.

Compared to the results for the single use of decorative paper, the increased improvement of the reflectance may be attributed to the polymer layer's thickness and the refractive index being well-matched with the SiO₂ layer and incident light [98], and to interference effects increasing the overall reflectance.

Although the best reflectance improvements were obtained with a 7.5 wt%, and colour being an important factor to consider, it was decided that the following studies would be done with the 5 wt% decorative paper.

SEM analysis was performed on the EG reference and 5 wt% samples (Figure 4.26). The SEM images of the EG 5 wt% sample indicate a more homogeneous surface than the

reference and, in view of the outer layer of the EG 5% sample being comprised of the exterior grade film (which contains PVDF/PMMA), the polymer conceals the nanoparticles below it.

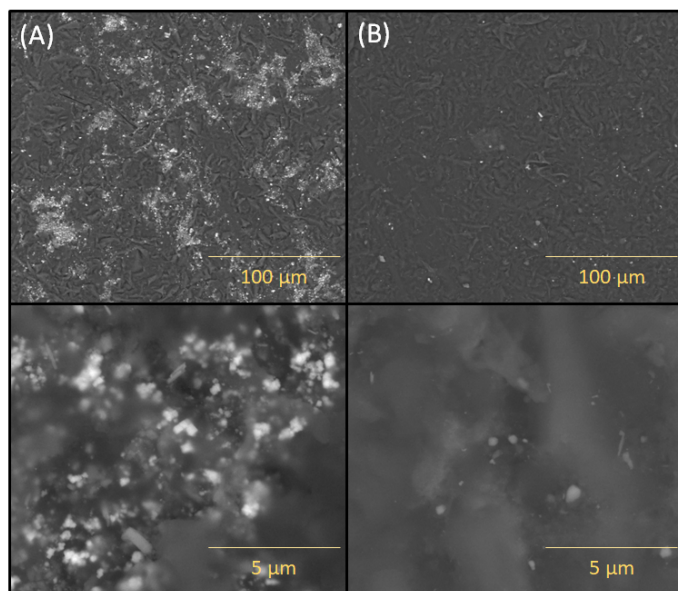


FIGURE 4.26: Scanning electron microscopy images of (A) reference and (B) EG 5 wt% samples. Magnifications: 5000 $\times$, 20 000 $\times$

4.4.2 Deposition of nanoparticles in the Exterior grade film

As shown in Figure 4.27, the deposition is visually noticeable when performed on the outer surface of the EG film. Therefore, only the 5 wt% and 7.5 wt% concentrations were studied. Additionally, the adhesion of the dispersion to the EG film is not as strong as in the case when the deposition is performed on impregnated paper.

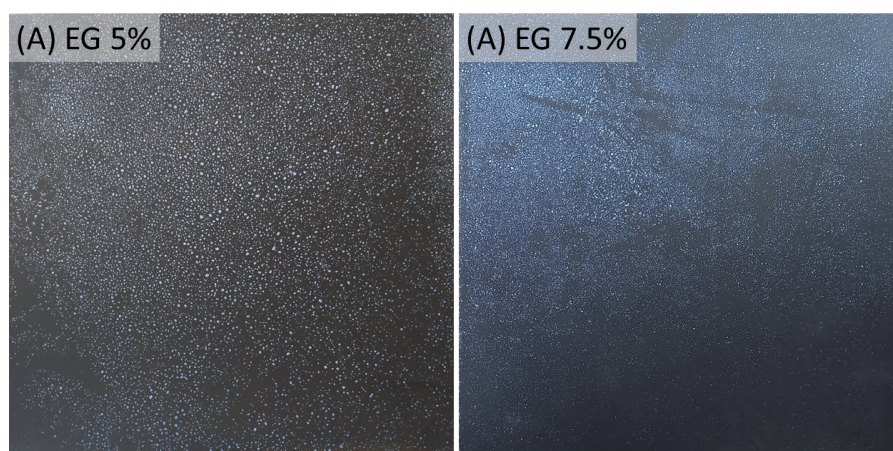


FIGURE 4.27: Samples with (A) Exterior grade film and decorative paper with (B) 5%, (C) 7.5% SiO_2 nanoparticles concentration.

Incorporating SiO₂ nanoparticles on the outer surface of the EG film improves the reflectance of the HPL (Figure 4.28A). Once again, the NIR and total reflectance of the 7.5 wt% sample (Table 4.6) are higher than the ones of the 5 wt% sample, and show larger improvements of reflectance in relation to the reference (35.5% and 28.4%, respectively). Nonetheless, for both samples, the reflectance is lower than the values obtained when the nanoparticles are deposited in the decorative paper (Table 4.5). Moreover, since the particles are well visible on the sample, the colour differences (Fig. 4.28B) are larger than in the previous case, and the 5 wt% sample reports a ΔE above the threshold.

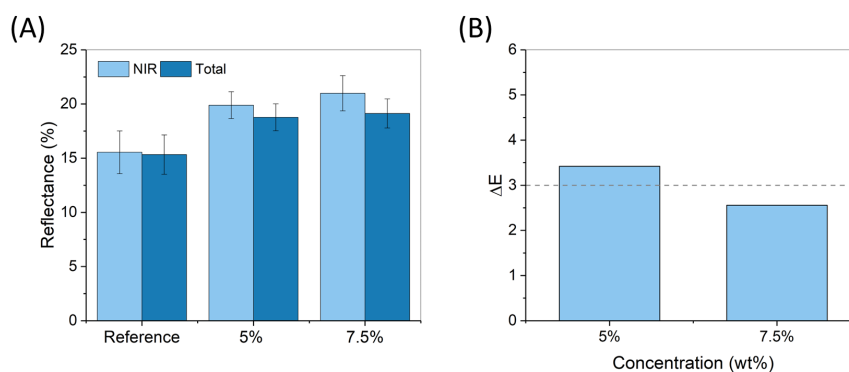


FIGURE 4.28: (A) Calculated total average and NIR reflectance and (B) colour differences of the HPLs with SiO₂-doped EG film.

Concentration (wt%)	R_{NIR}	R_{total}	ΔR_{NIR}	ΔR_{Total}
EG Reference	15.5 %	15.3 %		
5.0 %	19.9 %	18.8 %	28.4%	22.9%
7.5 %	21.0 %	19.1 %	35.5%	24.8%

TABLE 4.6: NIR (R_{NIR}) and total (R_{total}) reflectance values obtained for each SiO₂ 60-70 nm wt%.

4.4.3 Exterior grade film and decorative paper with PMMA

As stated in section 4.4.1, the simultaneous use of EG film and decorative paper with 5 wt% SiO₂ nanoparticles results in an optimal reflectance increase while maintaining acceptable colour differences. Accordingly, the 5 wt% SiO₂ dispersion in PMMA (EG SiO₂/PMMA) was sprayed on the decorative paper. Since the deposition was performed with a single spray gun, an additional sample with the nanoparticles dispersed in water (EG SiO₂/water) was studied.

The SiO₂/PMMA film was deposited via spray coating using a dispersion of SiO₂ and PMMA in acetone. The solvent evaporates after the deposition allowing a fast and large-area deposition on many substates. A drawback of the use of acetone as the solvent is that it easily evaporates at room temperature, causing a quick clogging of the nozzle's aperture. This entails that the spraying has to be done as promptly as possible, and as the opening clogs, the sprayed quantity is less consistent.

The spectral reflectance results (Fig. 4.29) show that the sample with SiO₂/PMMA has a higher reflectance compared to a dispersion in water. Using a single spray gun, with the use of a dispersion of nanoparticles in PMMA we obtain a greater increase of total and NIR reflectances (22.9% and 24.5%, respectively) compared to a dispersion in water for the same concentration (Table 4.7), as illustrated in Figure 4.30A. The nanoparticles are more easily dispersed in PMMA than in water, and, as a result, the more uniformly dispersed SiO₂ nanoparticles have stronger scattering abilities, achieving an improved reflectance. Also, the refractive index of SiO₂ matches the refractive index of PMMA ($n_{\text{SiO}_2} = 1.45$; $n_{\text{PMMA}} = 1.49$), ensuring the transparency of the film [98]. In addition, the reported ΔE values, ranging from 1.5 to 1.9, confirm that the doped-HPL can be considered colour-matched.

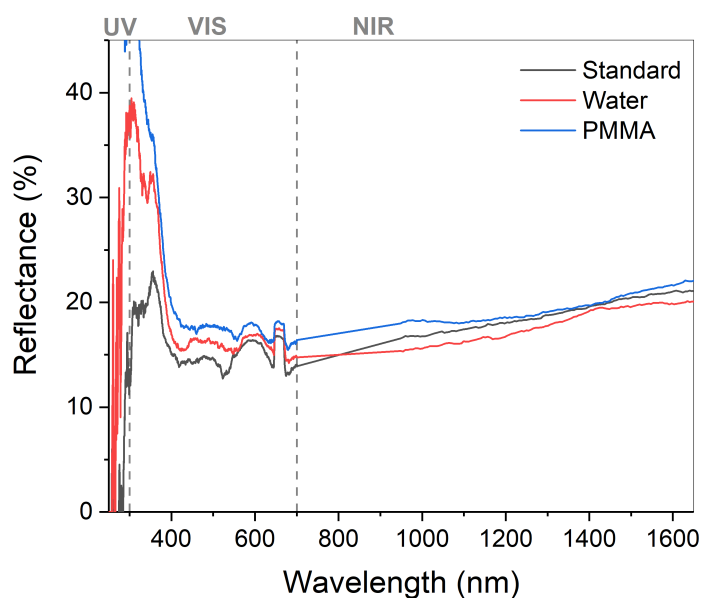


FIGURE 4.29: Spectral reflectance of the standard EG (black), EG SiO₂/water (red) and EG SiO₂/PMMA (blue).

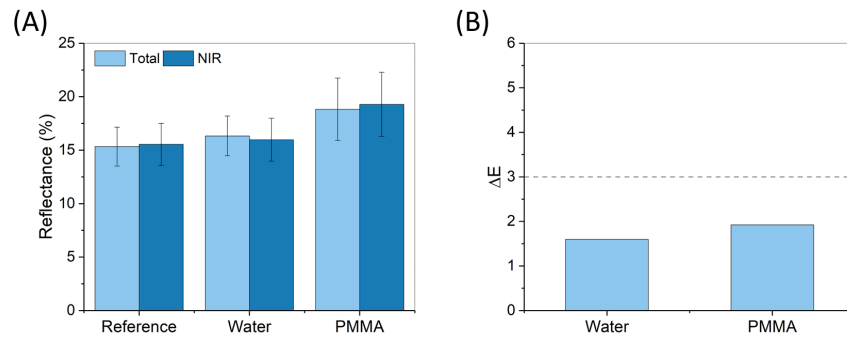


FIGURE 4.30: (A) Calculated total average and NIR reflectance and (B) colour differences of the EG SiO₂/PMMA and SiO₂/water samples.

Sample	R_{NIR}	R_{Total}	ΔR_{NIR}	ΔR_{Total}
EG Reference	15.5 %	15.3 %		
EG + PMMA 5 wt%	19.3 %	18.8 %	24.5%	22.9%
EG + water 5 wt%	16.0 %	16.3 %	3.2%	6.5%

TABLE 4.7: NIR (R_{NIR}) and Total (R_{Total}) reflectance values obtained for each sample.

In line with our results, which demonstrated a great improvement of the reflectance as well as satisfactory colour alterations, for a HPL with SiO₂ 60-70 nm particle content of 5 wt%, some studies have reported comparable results. In particular, a transparent film with 5 wt% SiO₂ 50 nm particles that showed the highest solar reflectance, as well as the best cooling performance, and a nanofiber membrane with 4 wt% SiO₂ nanoparticles that reached the best solar reflectance of 97.8%.

SEM images of the EG SiO₂/PMMA samples (Fig. 4.31) evidence a more homogeneous surface. SiO₂ nanoparticles are not detected, potentially owing to an improved distribution of the particles on the PMMA matrix and the EG film being on top of this deposited layer which affects the measurements.

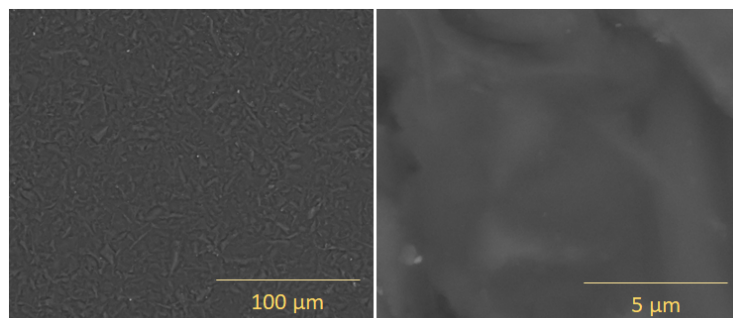


FIGURE 4.31: Scanning electron microscopy images of the EG SiO₂/PMMA. Magnifications: 1000 $\times$ and 20 000 $\times$

The FTIR spectrum of the samples EG PMMA 5% (blue), EG 5% (red) and EG REF (black) are illustrated in Figure 4.32. On all the samples, the absorption peaks observed from 8.6-8.7 μm are attributed to the CF₂ stretching vibrations of PVDF and/or the CH₂ bending vibrations of PMMA [99, 100]. This absorption peak is also assigned to Si–O–Si bonds, which explains the higher absorption displayed by both samples containing SiO₂. Both the EG 5% and EG PMMA 5% show peaks at 9.6-9.7 μm , which can correspond to Si–O–Si stretching [101] and CF₂ stretching vibrations of PVDF or to C–O of PMMA [99, 102], as well as a peak at 8.1 μm that may be attributed to Si–O bond [103], CF₂ stretching vibration of PVDF or the C–O–C stretching vibration of PMMA [99, 100]. The peak at 9.6-9.7 μm has a higher intensity for the EG 5% sample, while the EG PMMA 5% sample shows a higher intensity for the 8.1 μm peaks, which is likely associated to the PMMA intrinsic vibrations. Absorption peaks at 11.1 and 11.2 μm are observed on the EG REF and EG PMMA 5% samples and are assigned to C–C–C vibrations [104]. An additional peak at 12.9 μm is shown for the EG 5% sample, which is possibly linked to CH₂ rocking vibration of PVDF [99]. In the case of the EG REF, 10.4 μm and 12.4 μm peaks are attributed to the CH₂ rocking vibration [99], and the former can also be derived from C–H bonds of the melamine resin. Once again, the significant absorbance/emittance exhibited by the samples demonstrates a strong capability for energy release in the ATW.

The use of PMMA as the matrix has the intrinsic advantages of superior transmittance, low solar absorption and strong thermal emissivity in the ATW. Additionally, uniformly distributed SiO₂ nanoparticles can provide phonon polarization resonance, further improving the thermal emissivity of the radiative cooling film [98].

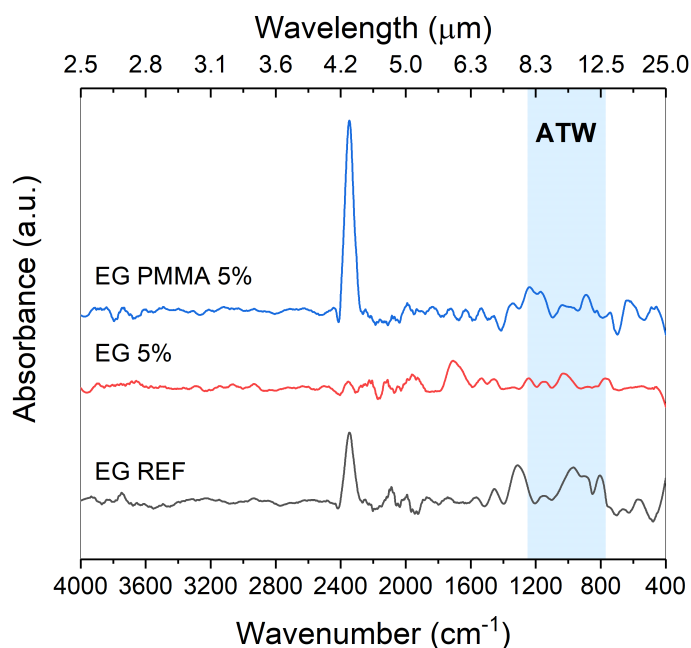


FIGURE 4.32: FTIR spectrum of EG PMMA 5% (blue), EG 5% (red) and EG REF (black).

4.5 Laminates characterization according to EN 438

4.5.1 Immersion in boiling water

The resistance to immersion in boiling water is a test with relatively extreme conditions, being a representative indicator of the samples enduring the extreme conditions stated in the standard, which were not performed here.

4.5.1.1 Overlay

The samples containing SiO₂ micro and nanoparticles and TiO₂ nanoparticles are presented in Figure 4.33. Both specimens with SiO₂ microparticles and TiO₂ nanoparticles exhibit small white dots after the test, possibly indicating agglomeration of the particles, with a rating 3 according to the rating scale at Table 3.1. As for the SiO₂ nanoparticles doped samples, no visual alterations are perceived, with a rating 5. It is worth noting that the reference sample, after the test, appears to have undergone slight visual alterations.

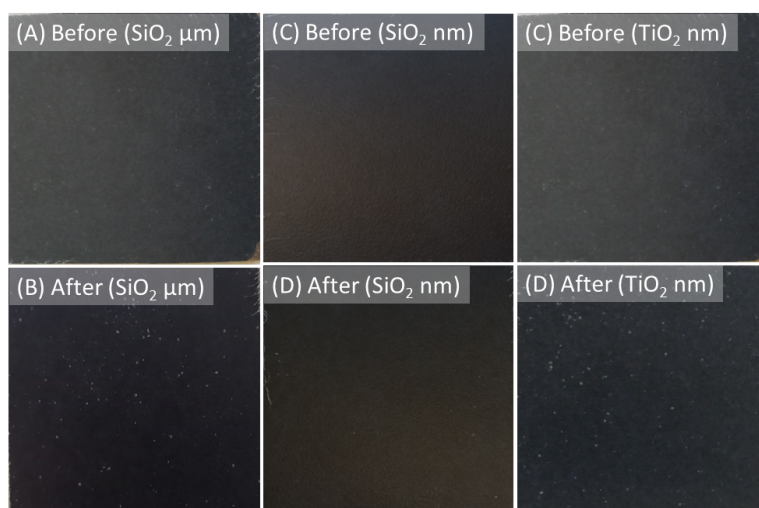


FIGURE 4.33: Specimens before and after immersion in boiling water: (A) and (B) SiO₂ microparticles, (C) and (D) SiO₂ nanoparticles, (E) and (F) TiO₂ nanoparticles

The alterations in mass and thickness after the test (Table 4.8) are below the established values, complying with the internal specifications at Surfoma.

Specimen	Δm	Δt
SiO ₂ 1 μm	4.11 %	5.86 %
SiO ₂ 60-70 nm	4.77 %	4.97 %
TiO ₂ 50 nm	6.13 %	7.31 %

TABLE 4.8: Mass and thickness increase after immersion in boiling water.

The reflectance of the specimens after the test was assessed to determine if the additional reflective properties were maintained after extreme conditions. After immersion in boiling water, the reflectance of the specimens incorporating SiO₂ 1 μm particles decreases (Fig. 4.34A). The SiO₂ specimens report a slight decrease of 4.6% in the NIR reflectance, in reference to the result before the test (Fig. 4.34B). As for the specimens with TiO₂ nanoparticles, the NIR reflectance value is unchanged. The VIS reflectance of the SiO₂ and TiO₂ nanoparticles doped specimens increases after the test, leading to improvements in the total reflectance of 1.6% and 4.3%.

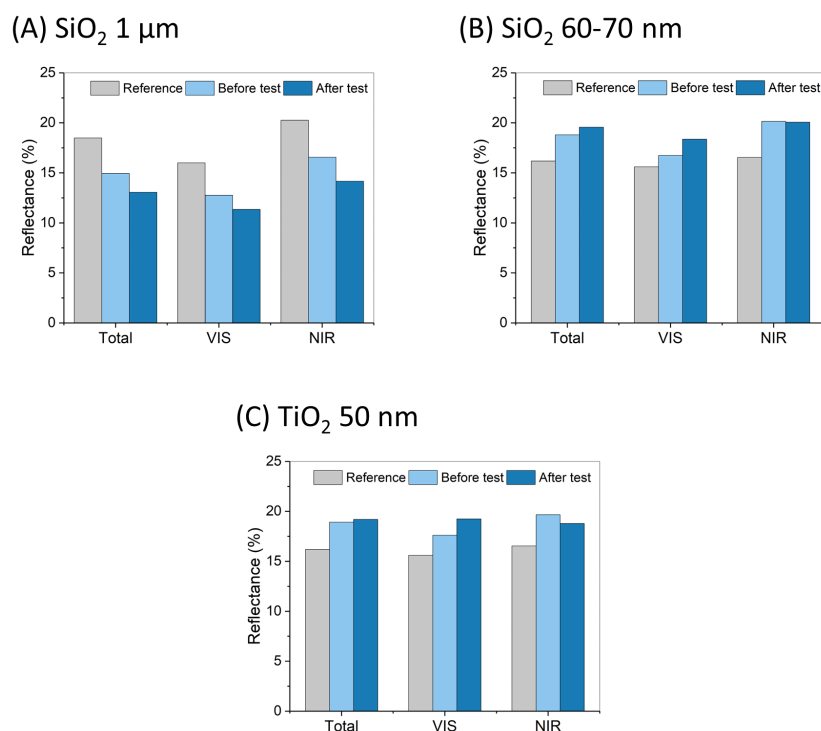


FIGURE 4.34: Reflectance of the specimens after immersion in boiling water with the deposition of (A) SiO_2 1 μm particles, (B) SiO_2 60-70 nm particles and (C) TiO_2 50 nm particles.

In both SiO_2 and TiO_2 specimens, the colour difference increases after the test. The TiO_2 -doped sample presents colour variations slightly above the threshold, while the colour differences obtained for the specimens with SiO_2 nano and microparticles are satisfactory (Fig. 4.35).

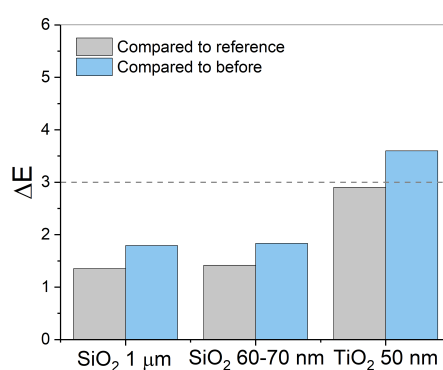


FIGURE 4.35: Colour difference of the specimens after immersion in boiling water doped with SiO_2 1 μm particles, SiO_2 60-70 nm particles and TiO_2 50 nm particles.

4.5.1.2 Decorative paper

Figure 4.36 depicts the samples containing SiO_2 and TiO_2 nanoparticles before and after the test. Since in the previous test, the mass and thickness increases were below the acceptable values, it was decided to only focus on the optical alterations suffered after the test. In this case, the specimens suffer fewer visual alterations after immersion in boiling water. The SiO_2 sample, once more, does not appear to have suffered any visual changes. The changes in the TiO_2 sample, although presenting some white dots, can be considered negligible.

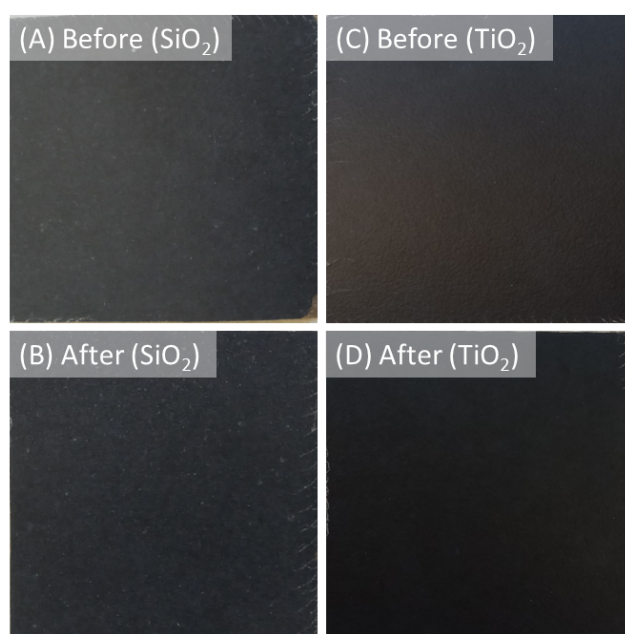


FIGURE 4.36: Specimens before and after immersion in boiling water: (A) and (B) TiO_2 nanoparticles and (C) and (D) SiO_2 nanoparticles.

Both the NIR (18.4%) and total (17.5%) reflectance of the SiO_2 specimen show slight increases (1.7% and 1.2%) with respect to the before the test results (Fig. 4.37A). After the test, the TiO_2 specimen reports a reduction in the NIR and total reflectance of 3.3% and 5.5% compared to the values obtained before the test (Fig. 4.37B). After the test, the colour differences obtained are not significant (Fig. 4.37C). Relative to the before results, the TiO_2 shows greater differences, considering that visual differences on the sample are detected.

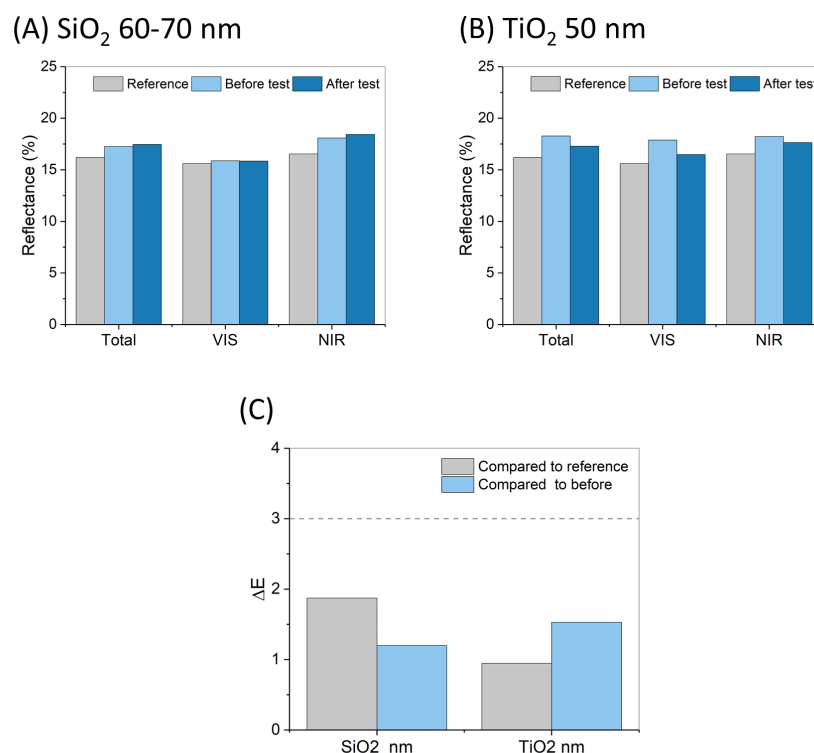


FIGURE 4.37: Reflectance of the specimens after immersion in boiling water with the deposition of (A) SiO₂ 60-70 nm particles and (B) TiO₂ 50 nm particles; (C) calculated colour differences of the SiO₂ 60-70 nm and TiO₂ 50 nm samples after immersion in boiling water.

4.5.2 Resistance to water vapour

After the resistance to water vapour test, the area of the specimen (Overlay SiO₂ 1 μm 2.5%) exposed to the water vapour presents slight brightness alterations (Fig.4.38), which corresponds to a level 4 (Table 3.1), satisfying the standard's requirements.

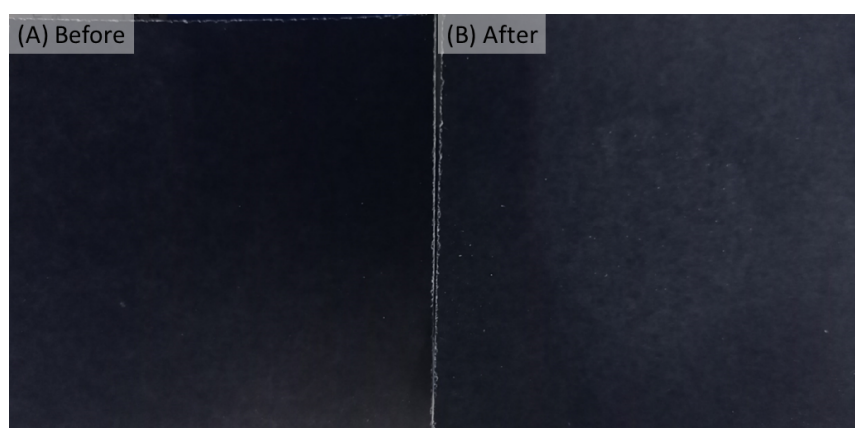


FIGURE 4.38: Samples (A) before and (B) after the resistance to water vapour test.

Considering that the sample showed minor alterations after the test, the remaining samples were not tested, and reflectance measurements were not taken.

4.5.3 Abrasion and scratch resistance

The SiO_2 1 μm 2.5 wt% sample was tested for both the abrasion and scratch resistance tests. Firstly, for the abrasion resistance test, given that after 400 revolutions, the kraft paper is still not visible despite the noticeable surface wear (Fig. 4.39A), the standard's requirements were complied. Regarding the scratch resistance test, a faint superficial scratch is visible with a 3 N load (Fig. 4.39B), being assigned a rating 3 classification, which satisfies the specifications required. Once again, because the samples fulfilled the standard's requirements, the remaining samples were not tested.

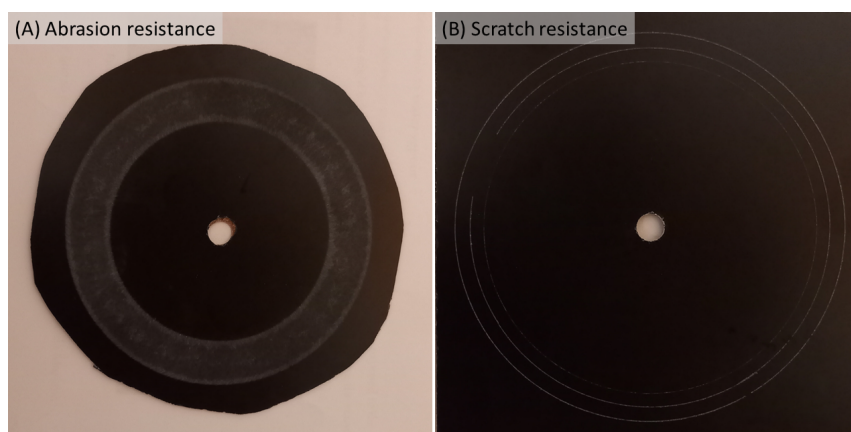


FIGURE 4.39: Samples after the (A) abrasion and (B) scratch resistance tests.

The samples constituted by the EG film did not undergo testing in accordance with EN 438 considering that they are still under development and given the time constraints.

4.6 Thermal behaviour evaluation

To investigate how the incorporation of solar reflective materials affects the temperature reached by the sample and the interior of a closed space, the thermal behaviour of the samples was evaluated.

4.6.1 Thermal behaviour measurements of the reference sample

The results of the experiments comparing the temperature of the reference sample (REF A) on box 1 and box 2 over time are shown in Figure 4.40. With all samples, time-dependent temperature measurements of the box's centre (T_C), bottom surface (T_{BS}) and top surface (T_{TS}) of the sample demonstrate a steep temperature increase within the initial 10 min after the IR lamp is turned on, followed by a gradual increase and then stabilization of the temperature after 30 min. The temperatures of the aluminium block (T_{Al}) are still increasing after 160 min. Throughout the duration of the measurements, the temperature of the centre and the aluminium block are identical in both boxes (Fig. 4.9A). Regarding the temperature of the T_{BS} and T_{TS} , the values obtained in box 2 are 2.59 °C and 2.58 °C above the temperatures reached on box 1 (Fig. 4.9C). To verify this behaviour, a second reference sample (REF B) was studied on both boxes. Comparing the results for REF B in the two boxes, the temperatures of the centre and the aluminium block are higher in box 2 (Fig. 4.40B). The T_{BS} and T_{TS} temperatures when the sample was placed on box 2 (Fig. 4.40D) were 4.58 °C and 3.87 °C above the temperatures obtained for box 1.

Overall, with both REF A and REF B, the temperatures obtained in Box 2 are higher than in the other box. This temperature difference is larger in the case of REF B. Considering that both samples studied are representative of a conventional HPL and that the boxes are identical, it would be expected that they would reach roughly the same temperature upon IR light exposure. At the temperature plateau, the mean temperatures of the aluminium block (T_{Al}), center of the box (T_C), bottom surface (T_{BS}) and top surface (T_{TS}), as well as the temperature differences between the two boxes (ΔT_{2-1}) of the samples REF A and REF B are presented on Table 4.9.

		T_{Al}	T_C	T_{BS}	T_{TS}
REF A	Box 1	39.02 °C	43.62 °C	52.77 °C	51.20 °C
	Box 2	38.79 °C	43.78 °C	55.36 °C	54.05 °C
	ΔT_{2-1}	-0.23 °C	0.17 °C	2.59 °C	2.85 °C
REF B	Box 1	36.51 °C	41.25 °C	47.79 °C	49.23 °C
	Box 2	38.24 °C	43.57 °C	54.09 °C	53.10 °C
	ΔT_{2-1}	1.74 °C	2.32 °C	4.30 °C	3.87 °C

TABLE 4.9: Mean temperature of plateau on the aluminium block (T_{Al}), center of the box (T_C), bottom surface (T_{BS}) and top surface (T_{TS}) and temperature difference between the two boxes (ΔT_{2-1}) of the samples REF A and REF B.

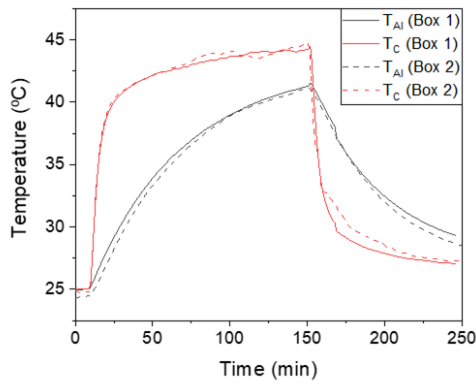
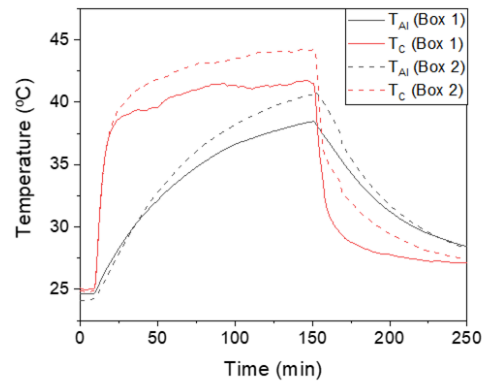
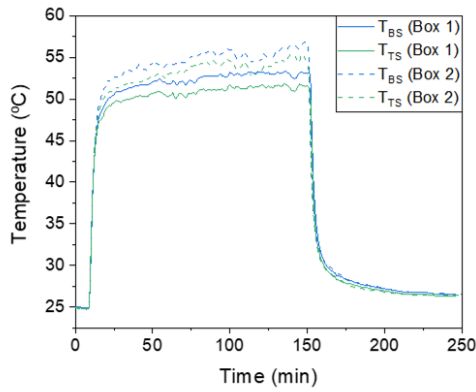
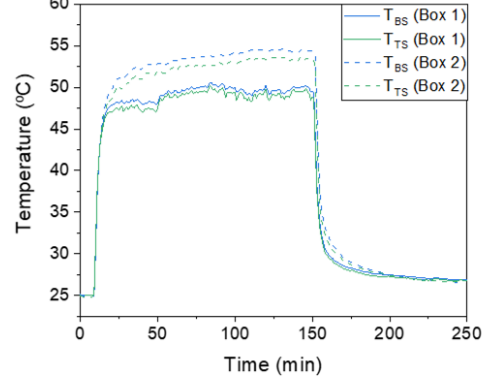
(A) REF A – T_{Al} and T_C (B) REF B – T_{Al} and T_C (C) REF A – T_{BS} and T_{TS} (D) REF B – T_{BS} and T_{TS} 

FIGURE 4.40: Time-dependent temperature of REF A and REF B by box.

To verify the reliability of the results and validate the temperature behaviour of the reference sample, two comparative tests were conducted with the sample placed in the same box. In the temperature plateau, the mean temperature differences obtained in the two consecutive tests for the same box are shown in Table 4.10. It is evident that the temperature differences obtained for the same box in the two comparative tests are considerable, thus revealing that the results are not reproducible.

	T_{Al}	T_C	T_{BS}	T_{TS}
ΔT_1	2.86 °C	3.34 °C	3.85 °C	6.20 °C
ΔT_2	4.77 °C	7.52 °C	9.21 °C	10.72 °C

TABLE 4.10: Mean temperature differences on the plateau of the aluminium block (T_{Al}), centre of the box (T_C), bottom surface (T_{BS}) and top surface (T_{TS}) of the REF sample on box 1 and box 2.

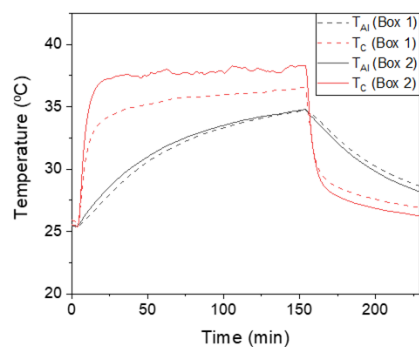
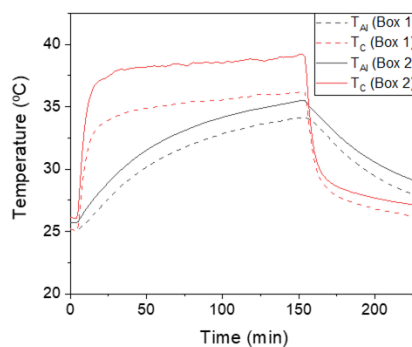
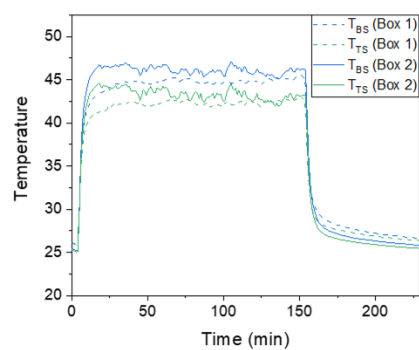
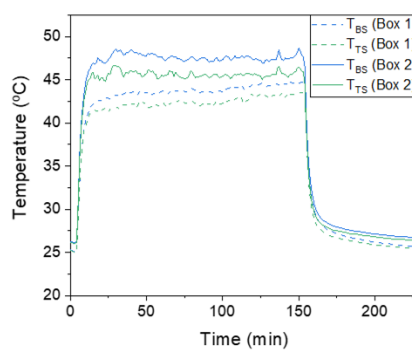
4.6.2 Thermal behaviour measurements of the EG PMMA/SiO₂ sample

Based on the previous tests, to evaluate the thermal performance of the EG PMMA/-SiO₂ sample, REF A was selected as the reference sample, since the temperature differences in the two boxes are lower.

Figure 4.41 shows the thermal measurements for the EG PMMA/SiO₂ sample and reference sample as a function of time, under the exposition of an IR lamp. It is evident that, similarly to the previous test, in each sample, the temperatures obtained in box 2 are higher than the ones for box 1. The mean temperature at the plateau of the samples EG PMMA/SiO₂ and REF are exhibited in Table 4.11. Contrary to expectations, on account of the two boxes leading to different results under the same conditions and using the same samples, further tests were not performed during this study.

		T_{Al}	T_C	T_{BS}	T_{TS}
EG PMMA/SiO ₂	Box 1	32.97 °C	35.70 °C	44.08 °C	42.74 °C
	Box 2	34.30 °C	38.69 °C	47.47 °C	45.57 °C
	ΔT_{1-2}	1.33 °C	2.99 °C	3.40 °C	2.83 °C
REF	Box 1	33.64 °C	37.91 °C	45.94 °C	43.03 °C
	Box 2	34.76 °C	40.46 °C	43.639 °C	42.38 °C
	ΔT_{1-2}	1.12 °C	2.55 °C	-2.31 °C	-0.65 °C

TABLE 4.11: Temperature of the aluminium block (T_{Al}), center of the box (T_C), bottom surface (T_{BS}) and top surface (T_{TS}) of the samples EG PMMA/SiO₂ and REF.

(A) REF – T_{Al} and T_C (B) EG PMMA/SiO₂ – T_{Al} and T_C (C) REF – T_{BS} and T_{TS} (D) EG PMMA/SiO₂ – T_{BS} and T_{TS} FIGURE 4.41: Time-dependent temperature of the samples, EG PMMA/SiO₂ and REF by box.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

The present work evaluated the optical and thermal performance of high-pressure laminates doped with solar reflective materials to assess the effect of this incorporation on the improvement of the energy efficiency of façades. The influence of different particles, sizes, and concentrations on the reflectance and colour of HPLs was studied. A thermal measurement setup was implemented to analyse the thermal behaviour of a standard HPL and an HPL with solar reflective properties.

NIR reflective materials (SiO_2 1 μm , SiO_2 60-70 nm and TiO_2 50 nm particles) were incorporated in a range from 0-5 wt% in different components of an HPL, namely in the overlay, decorative paper and exterior grade film. The incorporation of these materials in the overlay and in the decorative paper increased the reflectance of the HPL, which was valid for all the studied particles (Table 5.1). Moreover, the samples with the greatest increase in reflectance exhibited acceptable colour differences compared to a conventional HPL, indicating that the inclusion of dopants does not affect the colour significantly. An improvement of the reflectance with increasing particle concentration is observed with the SiO_2 nanoparticles in the range studied. In this case, the range of concentrations was broadened to 10 wt%, and the total reflectance continued to improve with the concentration, while the NIR reflectance was not further enhanced. Moreover, the colour differences between a reference and the SiO_2 -doped HPL were intensified with increasing concentration.

The production of HPL with an EG film was performed with the use of decorative paper doped with SiO_2 nanoparticles. Even though the greatest improvement of the NIR

and total reflectance (37.4% and 31.4% above the values for the reference sample) were obtained for the 7.5 wt% sample, the ΔE was above the threshold ($\Delta E = 4.1$). Therefore, the 5 wt% sample was the optimal sample, taking into consideration the reflectance and colour assessment ($\Delta R_{NIR} = 31.6\%$, $\Delta R_{Total} = 23.5\%$, $\Delta E = 1.5$). For this reason, PMMA/-SiO₂ 5 wt% dispersions were deposited on the decorative paper to produce an EG HPL, to evaluate if dispersing nanoparticles in PMMA leads to a more uniform distribution of particles and its influence on the optical properties. This resulted in a relative total and NIR reflectance improvement of 22.9% and 24.5% with a satisfactory $\Delta E = 1.9$.

		wt%	R_{NIR}	ΔR_{NIR}	ΔR_{total}	ΔE
Overlay	TiO ₂ 50 nm	2.5%	21.7%	31.5%	22-2%	2.8
Decorative paper	SiO ₂ 60-70 nm	5%	17.3%	20.1%	18.8%	1.6
EG	SiO ₂ 60-70 nm	5%	20.4%	31.6%	23.5%	1.5
		7.5%	21.3%	37.4%	31.4%	4.1
	SiO ₂ 60-70 nm PMMA	5%	19.3%	24.5%	22.9%	1.9

TABLE 5.1: Summary of the NIR and total reflectance, relative reflectance increases and colour differences obtained.

SEM characterization of the doped HPL revealed a non-uniform distribution of particles as well as aggregation, influencing the reflectance values achieved. FTIR-ATR analysis shows that the samples have additional absorbance/emittance properties in the atmospheric transparency window (from 8 to 13 μm) which is promising for the release of excess heat. The HPLs containing NIR reflective materials showed the potential to reduce the temperature increase of façades.

Regarding the thermal behaviour measurements, the first study was carried out to evaluate the behaviour of a standard HPL (reference sample). The implemented setup used two identical boxes to simultaneously compare two samples. It resulted that, under the same conditions, the reference sample reached different temperatures depending on which box it was placed, against expectations. This test was repeated for an equivalent reference sample, and the same behaviour was observed. The reference sample with the lowest temperature differences between both boxes was selected as the reference for a test with the EG PMMA/SiO₂ sample. Once more, for the same sample, the temperatures obtained in the identical boxes were distinct. Since the temperature measurements in

both boxes led to different results for the same sample and conditions, one could not conclude how incorporating NIR reflective particles in HPL could lower the temperature compared to a conventional HPL. As it is essential that the results are reproducible so one can simultaneously compare the temperature evolution of a doped and a reference sample, further thermal behaviour tests were not performed during this study.

5.2 Future Work

This study allowed us to reach innovative results regarding the incorporation of NIR reflective materials on HPLs, opening the door for more applications. This work would benefit from further testing, from the optical properties to the thermal behaviour.

Several approaches can be taken for the improvement of the reflectance of exterior grade high-pressure laminates. Given that a 7.5 wt% of SiO₂ nanoparticles lead to the greatest reflectance enhancement, a PMMA/SiO₂ 7.5 wt% (with the use of an EG film) should be prepared, to verify if an improved distribution of particles results in a better colour-matched sample. A promising approach to further improve the reflectance and the emittance is by using mixtures of particles with different sizes and/or different particles (e.g. SiO₂, TiO₂ and Al₂O₃) in order to cover a wider and more complete range of wavelengths in the solar spectrum and in the ATW. The use of dispersants to improve the particle's distribution should be considered while ensuring that these additives do not affect negatively the reflectance achieved.

One of the main challenges experienced was the implementation of a thermal behaviour evaluation measurement setup, in view of the results for the same sample not being the same for the tests in the two matching boxes, and different methodologies should be explored. Besides performing the tests under rigorous temperature and humidity conditions, the indoor measurement system can also be modified by installing a more stable setup by fixing the lamps and boxes. The solar absorption and heating of the inner side walls should be minimized, namely by attaching an aluminium tape to the outside of the chamber. It is worth considering preventing the inner ambient temperature inside the box from being too high, which can be done by drilling some holes in the outer wall of the structure. To minimize the convection caused by unexpected conditions, a low density polyethylene film can be attached.

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