



## FLORE Repository istituzionale dell'Università degli Studi di Firenze

# Thermo-optic durability of cool roof membranes: Effect of shape stabilized phase change material inclusion on building energy

Questa è la versione Preprint (Submitted version) della seguente pubblicazione:

Original Citation:

Thermo-optic durability of cool roof membranes: Effect of shape stabilized phase change material inclusion on building energy efficiency / Fabiani C.; Piselli C.; Pisello A. L.. - In: ENERGY AND BUILDINGS. - ISSN 0378-7788. - STAMPA. - 207:(2020), pp. 109592.1-109592.11. [10.1016/j.enbuild.2019.109592]

Availability:

This version is available at: 2158/1286093 since: 2022-10-26T17:48:01Z

Published version: DOI: 10.1016/j.enbuild.2019.109592

*Terms of use:* Open Access

La pubblicazione è resa disponibile sotto le norme e i termini della licenza di deposito, secondo quanto stabilito dalla Policy per l'accesso aperto dell'Università degli Studi di Firenze (https://www.sba.unifi.it/upload/policy-oa-2016-1.pdf)

Publisher copyright claim:

(Article begins on next page)

### Thermo-optic durability of cool roof membranes: effect of shape stabilized phase change material inclusion on building energy efficiency

C. Fabiani<sup>1</sup>, C. Piselli<sup>1,2</sup>, A.L. Pisello<sup>1,2</sup>

<sup>1</sup>CIRIAF - Interuniversity Research Centre, University of Perugia, Italy. Via G. Duranti 63 06125 Perugia (Italy) <sup>2</sup>Department of Engineering University of Perugia, Italy. Via G. Duranti 93 06125 Perugia (Italy)

#### Abstract

Cool roofs represent an acknowledged passive cooling technique aimed at reducing the amount of solar radiation absorbed by buildings and producing indoor overheating, particularly, in summer conditions. Cool roofs owe their unique behavior to improved thermo-optic performances which, however, have been shown to deteriorate when exposed to intense atmospheric weathering. In this context, the authors produced a shape stabilized composite with improved heat storage performance, by adding 15, 25 or 35 weight percentage of non-encapsulated phase change materials (PCMs) to the original blend of a liquid waterproof-polyurethane-based cool membrane. The behavior of such composite material, when exposed to accelerated temperature, humidity, and UV radiation cycles by means of standardized long-term weathering tests (QUV test), is investigated. The final aim of the study is to clarify if the PCM inclusion could help the membrane to better behave during the course of the time, because of thermal stress reduction. In order to do so, controlled atmospheric forcing and surface temperature continuous monitoring are used to investigate the degradation of the membrane produced by the imposed weathering stress. Results show that the introduction of 25% PCM in weight optimizes the superficial finishing characteristics of the prototype, allowing to maintain a more stable thermo-optic behavior, reducing both the thermal-induced degradation and the leakage phenomenon.

*Keywords:* Cool roofs, Phase change material, Shape stabilize material, Weathering analysis, QUV, Thermal energy storage in buildings,

Preprint submitted to Energy & Buildings

November 5, 2019

#### 1 1. Introduction

In the last decades, the awareness about the energy and environmental 2 role of the built environment to meet the European 2020 targets [1] has at-3 tracted the focus of researchers [2]. Several solutions for building energy efficiency were developed and acknowledged [3]. In particular, the energy 5 consumption for cooling has been gaining attention due to the raising use of 6 active cooling systems for contrasting the overheating associated to climate 7 change and urban development [4]. Indeed, a worldwide increase of cooling 8 degree days was demonstrated [5]. Therefore, the introduction of passive 9 cooling techniques, capable of reducing summer overheating phenomenon, 10 could play a significant role in the achievement of the global energy con-11 sumption reduction targets [6]. Such mitigation and adaptation strategies 12 are effective both at the building scale and at the district or city scale for the 13 restoration of natural passive cooling [7]. Among passive cooling strategies, 14 cool materials are capable to induce a negative radiation forcing by reflecting 15 the shortwave radiation back to space [8]. Therefore, they allow to counter-16 act the global warming, cooling down urban heat islands [9], and reduce the 17 cooling energy use and the associated demand for power, consumption of fuel, 18 greenhouse gas emissions, and air pollutants in buildings [10]. In details, di-19 rect energy savings and emission reductions can be achieved thanks to the 20 reduction of envelope solar heat gains [11, 10], while indirect savings from 21 reducing the air temperature difference across the building envelope [12, 13]. 22 In particular, cool roofs were demonstrated to save annual energy consump-23 tion in all buildings needing for cooling, with negligible heating penalties 24 in winter, precluding the need to install any air conditioning system under 25 certain boundary conditions [14]. For instance, Herná ndez-Pé rez et al. [15] 26 showed a daily heat gain reduction through the roof up to about 80% thanks 27 to a cool coating with respect to a conventional roof. Moreover, bismuth 28 titanate (BTO) was demonstrated to be a potential cool pigment with even 29 higher reflectance property than the conventional  $TiO_2$  pigment, for energy 30 saving applications [16]. 31

On the other hand, the proper inclusion of phase change materials (PCMs) in the building envelope as passive thermal energy storage application enhances its energy storage capability [17, 18]. Therefore, indoor thermal

conditions are improved by balancing the environmental temperature and 35 dampening its fluctuation [19]. In this view, one of the main technical is-36 sues is how to effectively integrate such material within the building envelope 37 [20], while preventing leakage and volatilization and ensuring material con-38 servation [21]. To solve this problem, shape-stabilized PCMs is one of the 39 methodologies currently being used for encapsulation [22]. It consists on the 40 fixation of the phase change material within a matrix, by blending it with 41 a suitable polymer, which results in the suppression of leakage in the liquid 42 phase [23]. Different shape-stabilization procedures were tested for various 43 applications, e.g. a form-stable composite using diatomite (a type of natural 44 non-metallic mineral material) as supporting material [24]. This procedure 45 can be effectively implemented also by coupling cool roof materials and PCMs 46 [25, 26]. The combination of high reflectivity and phase change materials 47 for the building envelope has been narrowly studied, showing potentialities 48 both for building energy efficiency [27] and urban heat island phenomenon 49 mitigation [28]. Lu et al. [29], for example, developed and experimentally 50 monitored a novel roof coupling a PCM-eutectic mixture layer (homogeneous 51 mixture of two materials) and a cool roof coating, which showed a smoother 52 temperature fluctuation and higher thermal insulation with respect to the 53 simple cool roof. Focusing on cool roof coating thermal stress reduction, 54 Saffari et al. [30] defined the optimum PCM melting temperature to reduce 55 cool roof membrane thermal stress, while minimizing building annual energy 56 needs in different climate zones worldwide. 57

Nevertheless, the demonstrated benefits achievable by such strategies can 58 be compromised during their life span due to material aging associated to 59 weathering [31], soiling [32, 33, 34], and biological growth [35]. Although 60 albedo changes induced by weathering, they can be reduced by an accurate 61 maintenance procedure, e.g. wiping, rinsing, and washing [36]. However, the 62 same technique is not as effective in reducing natural weathering alterations. 63 Additionally, although cool materials aging seems not to represent a barrier 64 for their energy efficiency, performance loss over time must be understood 65 [37]. Several studies quantified the effect of natural exposure on solar re-66 flectance [38, 39]. For instance, Ferrari et al. [40] analyzed the influence of 67 natural aging on the solar reflectance of clay roof tiles. 68

De Masi et al. [41] found, through in-field test, that the solar reflectance of an acrylic white paint for cool roof applications can decrease from 0.67 to 0.48 after 1 year of exposure to the outdoor environment. Similarly, Aoyama re t al. [42] demonstrated the increased durability due to the self-cleaning

capability of a high-reflectance coating subjected to outdoor exposure test. 73 However, such in-field tests require long-time exposure to provide interesting 74 results. Therefore, accelerated weathering techniques, such as QUV test [43], 75 have been developed to provide a shorter test period. In such a test, materi-76 als are alternately exposed to temperature cycling, UVA radiation, and water 77 condensation to accelerate natural environments with higher stress, without 78 changing the failure mechanism [44]. The QUV test is typically used to assess 79 materials mechanical failure, but it can also be used to predict the variation 80 in the thermo-optical performance of materials [45]. Since no unequivocal 81 correspondence can be established between accelerated and real weathering 82 due to the large variability on the possible local boundary conditions, real 83 exposure is generally preferred to the accelerated one. However, QUV anal-84 ysis can produce acceptable information in terms of comparative behavior of 85 the investigated products with a lower effort in terms of experimental time. 86 Santunione et al. [46], for instance, assessed the capability of an acceler-87 ated test method to investigate the consequences of biological aggression on 88 coating materials. 89

To verify the durability of materials thermal-energy performance before 90 and after the aging process, dynamic analysis can be carried out in controlled 91 conditions [47]. This procedure allows to investigate the dynamic behavior of 92 building materials and components with a better reliability than real building 93 applications, frequently affected by extra-variables such as occupancy [48]. 94 Ricciu et al. [49] used this methodology for the thermal characterization 95 of different insulating materials, compared to more traditional procedures, 96 while D'Alessandro et al. used it to characterize the thermal buffer capabil-97 ity of innovative PCM-doped concretes for structural applications [50]. In 98 order to assess the performance of PCM-doped cool roof tiles, Chung and 99 Park [51] simulated summer weather conditions in an artificial environment. 100 The measurements enabled to demonstrate the capability of PCM to further 101 reduce roof external surface temperature, while improving indoor thermal 102 comfort throughout the year. 103

Based on the above, a novel composite material combining polyurethane liquid waterproof-polyurethane-based cool membrane with different percentages of non-capsulated PCMs was developed for roof applications [52, 26]. When combining PCMs and cool roofs, exposure to sun, rain, and wind are critical factors to be taken into account, since they significantly influence the thermo-mechanical response of the membrane, determining the detrimental leakage phenomenon. Therefore, the composite material was exposed to

accelerated weathering long-term tests (QUV test), to assess the cool mem-111 brane vulnerability to real environmental forcing. In a previous paper [45], 112 the same authors evaluated the influence of PCMs inclusion, on the durabil-113 ity of the cool membrane mostly in terms of thermal properties, morphology, 114 and mechanical response. Following up from these studies, the purpose of 115 this work is to further analyze the capability of PCMs to preserve the cool 116 membrane thermal-energy performance over time, due to thermal stress re-117 duction. In detail, thermo-energy dynamic-analysis of the aged composite 118 material was developed in a controlled environmental chamber to assess the 110 role of the PCM in reducing the PCM-doped cool roof surface temperature 120 [48, 50].121

#### 122 2. Materials and sample preparation

In this work, the long-term durability of a polyurethane-based-white-123 liquid membrane for non-sloped roof applications developed by the authors 124 in a previous research work [52, 26] is experimentally investigated. The afore-125 mentioned membrane is optimized by using titanium dioxide ( $TiO_2$ , in the 126 form of rutile) and hollow ceramic micro-spheres, to increase its passive cool-127 ing potential. Additionally, an organic paraffin with a melting point of 25 128  $^{\circ}$ C and a heat storage capacity of 148 kJ·kg<sup>-1</sup> is also introduced within the 129 mixture, with the aim of preserving better spectral reflectance in the near 130 infrared region of the solar spectrum. Additionally, the smallest possible al-131 teration during the course of accelerated weathering (QUV) tests together 132 with the maintaining of the required flexibility and superficial finishing char-133 acteristics, was also sought. 134

135

The prototype membranes were produced by simply mixing the solid-state 136 non-encapsulated paraffin within the membrane tank with liquid polyurethane. 137 while keeping an ambient temperature of 20  $^{\circ}$ C to prevent the PCM from 138 melting during this phase. In the previous works, three different specimens 139 were produced, i.e. a reference "pure-cool" membrane with no additives 140 (noOPT), a cool membrane with "optimized-cool" surface (OPT) and three 141 cool membranes with 15%, 25%, and 35% in weight of PCM added to the 142 original mix design with titanium dioxide and the micro-spheres, i.e. 15PCM, 143 25PCM and 35PCM, respectively (see Figure 1). 144

145

Here, only the optimized-cool and the three PCM-doped membranes were selected to perform a durability investigation of the prototypes against temperature and radiation-induced mechanical stresses. In particular, four square samples with the dimension of 10 cm×10 cm were collected for every considered membrane, and exposed to different accelerated weathering times, i.e. 0, 15, 30 and 60 days.



Figure 1: Investigated polyure thane membranes: (a) OPT, (b) 15PCM, (c) 25PCM, and (d) 35PCM, before the accelerated weathering procedure.

#### 152 3. Experimental methodology

As reported in Figure 2, the research procedure consisted of the following
 main steps:

- development of the proposed cool roof solution through the integration
 of an organic PCM, i.e. paraffin-based material, into the polyurethane based cool membrane in different percentages [52, 26];

- accelerated weathering procedure of the different membranes according
 to ASTM D 4329-99 (Standard Practice for Fluorescent Ultraviolet

- (UV) Lamp Apparatus Exposure of Plastics) [53] and ASTM G154 06 (Standard Practice for Operating Fluorescent Light Apparathus for
  UV Exposure of Nonmetallic Materials) [54];
- surface characterization of the membranes in terms of spectral near
   normal-hemispherical reflectance according to ASTM E903-12 (Stan dard Test Method for Solar Absorptance, Reflectance, and Transmit tance of Materials Using Integrating Spheres) [55];
- thermal characterization of the membranes at different aging times, i.e.
   non-aged, 15, 30, and 60 days of aging using the sol-air temperature (T<sub>Sol-air</sub>);
- $\begin{array}{rcl} & & \mbox{ thermal characterization of the non-aged membranes using a halogen} \\ & & UV\mbox{-lamp and comparison with the profiles from the sol-air temperature} \\ & & (T_{Sol-air}) \mbox{ analysis.} \end{array}$



Figure 2: Schematic representation of the main steps carried out in this work

#### 173 3.1. Accelerated weathering test

The accelerated aging test was carried out by usign a QUV machine (QUV Accelerated Weathering Tests, Q-Lab) and according to the international standards ASTM D 4329-99 [53], linked to the operative procedure described in the ASTM G154-06 [54]. The samples were repeatedly exposed to the following forcing conditions:

- 8 hours of UVA radiation (340 nm, energy of 0.77  $W \cdot m^{-2}$ ) at 50 °C;
- 2 hours in humid condition (100 RH%) at 40 °C;
- -2 hours in humid condition (100 RH%) at 20 °C.

According to ASTM G154-06 standard, any exposure conditions, pro-182 vided that they are fully described, may be used in the investigation pro-183 cedure. All this considered, the conditioning cycle used in this work was 184 specifically designed by the authors in order to reproduce environmental con-185 ditions that could be representative of the peak temperature and humidity 186 conditions characterizing climate areas where cool roof solutions are typically 187 recommended and applied as passive cooling systems for building energy ef-188 ficiency. 180

190

The effect of the accelerated weathering test on the different samples of cool membranes was evaluated after 15, 30, and 60 days of exposure, based on the common practice derived from the two reference ASTM standards [53, 54]. More in detail, three samples per type were exposed to the test. The first series of samples, one for each type (OPT, 15PCM, 25PCM, and 35PCM), was extracted out of the machine after 15 days, the second series was extracted after 30 days, and the last series was extracted after 60 days.

#### <sup>198</sup> 3.2. Spectral near normal-hemispherical reflectance

The in-lab optical characterization of all the samples was carried out by 199 means of a Solid Spec 3700 UV-vis-NIR spectrophotometer equipped with a 200 60 mm integrating sphere coated with barium sulfate, in the range 300–2500 201 nm according to the ASTM E903-12 [55] standard method. Five different 202 spectral near normal-hemispherical reflectance measurements were taken for 203 each of the 16 samples, by measuring different geometrical positions on the 204 membranes, in order to produce a reliable statistic representation of the optic 205 behavior of the innovative coatings. 206

#### 207 3.3. Thermal monitoring in real dynamic conditions

The thermal characterization of the membranes was carried in two different stages. First, each membrane was exposed to a hygro-thermal conditioning cycle using the sol-air temperature. Secondly, the non-aged samples were exposed to an additional hygro-thermal forcing procedure, making use of a solar simulator to reproduce the incoming radiative flux. The former procedure was aimed at evaluating the differential response of the membranes after different aging times; the latter, at comparing the thermal profiles produced using the sol-air temperature (defined in more details in the following) with the ones registered using the solar simulator.

Both analyses were carried out using an ATT DM340SR climatic cham-217 ber equipped with a test compartment ( $601 \text{ mm} \times 810 \text{mm} \times 694 \text{ mm}$ ) where 218 it is possible to obtain a temperature- and humidity-controlled environment 219 in the range  $-40-180 \text{ }^{\circ}\text{C} \pm 0.5 \text{ }^{\circ}\text{C}$  and  $10-98\% \pm 3\%$  of RH [56]. The chamber 220 is also equipped with a solar simulator, i.e. a halogen lamp operating in 221 the power range 600 to 1200 W (solar spectrum shown in Figure 3), and 12 222 PT-100 temperature sensors. The environmental chamber ensured the high 223 stability of the tests, compared to field experiments, and the repeat ability 224 of the same experiments for bench-marking purposes. 225

226



Figure 3: Spectrum of the solar simulator (halogen lamp) compared to the AM 1.5 direct solar spectrum from ASTM G173–03(2012) (Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface) [57]).

During the experimental campaign, each type of membrane was housed within the controlled environment of the climatic chamber, and exposed to specifically designed environmental cycles. More in detail, real meteorological data from a weather station located on the rooftop of a University building located in central Italy (Perugia) were used to investigate the effect of the
selected phase change materials on the long-term durability of the advanced
cool roof membranes. In particular, weather data from a typical hot summer
day, i.e. 2017-07-26, were selected to be reproduced within the simulated
environment of the climatic chamber (see Figure 5).

236

During the experimental campaign, the membranes were placed in a specifically designed polyurethane (PUR) sample holder, assembled in order to completely protect and insulate five surfaces out of six, i.e. the four sides and the bottom surface, while leaving the upper one exposed to the controlled environment of the chamber (see Figure 4).

10 T-type thermocouples were shielded with an aluminum tape and used 242 to monitor the thermal behavior of each sample. In particular, five T-type 243 sensors were attached at the upper surface of the membranes, while the re-244 maining five probes were placed at the bottom surface, as shown in Figure 245 4. The thermocouples were connected to a data acquisition system model 246 cDAQ-9184 equipped with two NI 9213 Spring slots from National Instru-247 ments, and programmed in order to read the sensors every 30 seconds. In this 248 way, it was possible to (i) accurately register the surface thermal profile of 249 the roof membranes and (ii) identify the effect of the PCMs throughout the 250 thickness of the samples during the overall extent of the monitoring process. 251 252

#### 253 3.3.1. Sol-air temperature-based cycles

In the first stage of the thermal analysis, each membrane was exposed to a specifically designed, sol-air temperature-based forcing cycle (Tsol cycle), reproducing the local boundary conditions between 6:00 AM and 9:00 PM Local Standard Time (LST).

The Tsol cycle, makes use of the sol-air temperature  $(T_{Sol-air})$  to combine temperature and radiative contributions in one single temperature forcing parameter, to be used in combination with the relative humidity profile.

In this case, a broader time interval (between 5:00 AM and 8:00 PM (LST)), was selected. The sol-air temperature for the horizontal roof stratigraphy exposed to the selected weather conditions was computed according to Equation 1 [58]:

$$T_{\rm Sol-air} = T_{\rm air} + \alpha I_{\rm g} R_{\rm se} - \Delta Q_{\rm ir} R_{\rm se} \tag{1}$$



Figure 4: Schematic representation of the experimental setup.

where  $T_{\rm air}$  is the outdoor air temperature from the weather file (°C);  $\alpha$  is the solar absorptance of the specific membranes;  $I_{\rm g}$  is the global solar radiation from the weather file (W·m<sup>-2</sup>); R<sub>se</sub> is the external surface resistance (m<sup>2</sup>·(K·W)<sup>-1</sup>); and  $\Delta Q_{\rm ir}$  is the correction to infrared radiation transfer between surface and environment if sky temperature is different from T<sub>air</sub>, (W·m<sup>-2</sup>).

The term  $R_{se}$  Equation 1, was set to 0.04  $(m^2 \cdot K^{-1} \cdot W^{-1})$ , in accordance to the recommendations of ISO 6946:2017 (Building components and building elements – Thermal resistance and thermal transmittance – Calculation methods) [59]. As for the infrared radiation transfer correction, since the roof membrane respresents a upward-facing surface in real applications,  $\Delta Q_{ir}R_{se}$ was imposed to its maximum value, i.e. 3.9 °C [60].

277

Given that the sol-air temperature depends on solar absorptance, which differs by material, each membrane was separately analyzed and exposed to a unique temperature profile based on its solar absorptance. All the membranes were assumed to be opaque surfaces, therefore, the specific solar absorptance of each surface was calculated as  $\alpha = 1 - \rho$ , making use of the reflectance



Figure 5: Relative humidity, air temperature, and global radiation (in the range 300 – 2800 nm) values registered by the weather station at Perugia University on July 26, 2017.

values presented in Section 4.1.

#### 284 3.3.2. Radiation-based cycles

At a later stage, the non-aged membranes were exposed to an additional environmental cycle (the air temperature-radiation based – TaRAD – cycle), which was designed to exactly reproduce the local climatic conditions in terms of outdoor air temperature, relative humidity, and global radiation flux on the horizontal surface from 7:30 AM to 5:30 PM (LST). This specific time range was selected due to technical limitations: the solar simulator only allows to reproduce radiative fluxes above 250 W·m<sup>-2</sup>.

In contrast to the sol-air temperature-based thermal analysis, the investi-292 gation procedure carried out using air temperature and radiative flux as two 293 separate boundary conditions allows to simultaneously analyze the thermal 294 behavior of each type of membrane. In this case the surface interaction be-295 tween the incoming radiation and the material is a real physical phenomenon 296 occurring during the simulation. Therefore, every membrane behaves in a 297 different way, based on its own thermo-optic properties, although exposed to 298 the same conditioning cycle. 290

300

All this considered, using solar simulators could significantly reduce experimental time. However, solar simulator are often associated to nonnegligible deviations in terms of short-wave radiation accuracy, and lack of long-wave radiative exchange with the sky. In this view, the main purpose of this analysis is to compare the thermal profiles produced using sol-air temperatures with the ones registered using the solar simulator and evaluate the actual deviation between these conditioning techniques.

#### **4. Results and discussions**

#### 309 4.1. Thermo-optic performance of the roof membranes

Results from the solar reflectance measurements as a function of the aging 310 procedure are plotted in Figure 6. As can be seen, at time zero, the non-aged 311 optimized membrane (OPT sample) presents the highest solar reflectance. 312 Despite this, as demonstrated in a previous contribution from the same au-313 thors [26], the introduction of the PCMs does not result in chemical variations 314 of the original polyurethane-based substrate. On the contrary, the two com-315 ponents maintain their properties and coexist in a stable form, preserving 316 and globally combining their unique behavior. As a consequence, the exter-317 nal finishing of the membrane is really constituted by the only polyurethane 318 matrix, at least, until the PCM finally leaks out of it reaching the surface. 319 The introduction of the latent doping agent, however, increases the com-320 posite surface roughness, due to the presence of PCM agglomerations right 321 beneath the surface. 322

As a consequence, larger shadows are produced and lower reflectances are obtained with increasing PCM percentages [61]. Said reduction is particularly large in the case of the 35PCM sample, which reaches a reflectance of 0.51, before aging.

327

By focusing on the long-term performance of the investigated membranes, 328 and assuming a good correlation between accelerated weathering and natural 329 exposition effect, a different resilience capability can be observed. The QUV 330 aging test seriously affects the optimized membrane, which significantly re-331 duces its reflectance with increasing weathering times (according to a quite 332 reasonable linear trend). As for the 15PCM sample, namely the one with the 333 minimum PCM addition, Figure 6 shows a much less stable trend, character-334 ized by an abrupt reflectance decrease after 15 days of aging, while after 30 335

and 60 days, similar performance compared to the pure membrane are found.
Globally, the introduction of the PCM reduces the slope of the linear fitting
curve connecting the reflectance measurements at different aging times. This
brings the 15PCM sample to obtain a comparable reflectance with respect
to the optimized membrane after 60 days aging.

Concerning the 25% PCM-doped solution, this particular PCM concentration shows the most promising long-term performance. The slope of the 25PCM fitting line, indeed, tends to zero in this case.

As for the 35% PCM-doped solution, the highest reflectance reduction is observed in the long-term weathering. As shown in Figure 6, the 35PCM sample solar reflection capability is initially increased, and only finally drops to 0.47 (after 60 days aging).

348

Furthermore, it should be stressed that both the 25PCM and the 35PCM sample experience an initial reflectance increase. This is probably caused by a positive superficial smoothing, produced by the QUV forcing cycles that reduces the drop shadows effect.



Figure 6: Total solar reflectance for the investigated polyurethane membranes, i.e. OPT-CM, 15PCM-CM, 25PCM-CM, and 35PCM-CM, before and after the accelerated weathering procedure.

Based on the above, we can state that each membrane is differently af-353 fected by the QUV test. Figure 7 shows the typical forcing profiles for a 354 single aging day. As can be seen, during the weathering procedure each sam-355 ple experiences abrupt variations in terms of temperature, relative humidity, 356 and UVA radiation. Such variations produce intense temperature gradients 357 and, consequently, the development of non-negligible stresses and strains in 358 the polyure than e substrate, resulting in a complex micro-cracking pattern 359 that globally concurs to reduce the reflectance of the OPT sample. 360

361

The introduction of PCMs, being capable to store part of the heat in 362 the latent form, is expected to reduce such temperature gradients and the 363 albedo degradation with it. However, only the 25PCM sample maintains a 364 higher reflectance throughout the aging. This suggests that PCM concentra-365 tions around 15% and 35% do not allow the latent additive to fulfill its buffer 366 task. In particular, it seems that lower PCM concentrations do not guarantee 367 enough energy density to overcome the detrimental mechanical deterioration 368 of the substrate, which consequently experiences a similar thermally-driven 369 micro-cracking process. Therefore, as experienced by a direct visual and tac-370 tile inspection, the liquid PCM leaks out of the membrane already after 15 371 days aging, reducing its surface reflectance. 372

Higher concentrations, on the other hand, initially allow to produce the expected buffering effect. However, on the long-term the 35PCM sample experiences a similar drop in reflectance to the one found in the 15PCM after 15 days. This, together with the results from the visual and tactile inspection, suggests that leakage eventually occurs also in this case, but only at a later stage and most probably because of the higher PCM concentrations in the composite.

As a consequence, in the long-term, despite the occurrence of different deterioration mechanisms, both the 15PCM and the 35PCM, mostly behave as the OPT membrane.

# 4.2. Effect of phase change materials on the surface temperature of the aged cool roof membranes

Figure 8 shows the comparison among different surface temperature profiles monitored during the imposed Tsol cycles for each kind of membrane and weathering time. In particular, profiles with the same QUV exposure time are grouped and plotted on the same panel, allowing us to compare



Figure 7: Forcing profiles for a typical QUV aging day.

the differential thermal response of the membranes when exposed to similar weathering conditions.

As expected, at time zero the TiO<sub>2</sub>-optimized membrane with no PCM 391 addition produces the lowest surface temperature profile, exceeding 40 °C 392 only in the central part of the day (between 11:45 AM and 1:27 PM (LST), 393 as shown in Figure 10 and Table 1). Concerning the three considered PCM-394 doped solutions, according to the previously described solar reflectances, an 395 increased temperature trend is produced when increasing the weight percent-396 age of the latent additive in the roofing membrane. However, no significant 397 difference can be seen between the 25 and the 35% PCM solution. After 15 398 days of accelerated weathering, the reference optimized membrane with no 390 PCM suffers by a non-negligible temperature increase, featuring a wider tem-400 perature bell with a peak value of 45.3 °C versus the 41.2 °C registered before 401 the aging process. Additionally, Figure 10 shows that the 15-days-aged op-402



Figure 8: Comparison among the different superficial temperature profiles from the Tsol cycles considering the same accelerated weathering time, i.e. (a) 0 days, (b) 15 days, (c) 30 days, (d) 60 days.



Figure 9: Change in surface temperature of the considered membranes, i.e. (a) OPT, (b) 15PCM, (c) 25PCM, (d) 35PCM, when exposed to 15, 30, and 60 days of accelerated weathering procedure with respect to the maximum air temperature difference registered in the selected day ( $T_{aged} - T_{non-aged}$ ) / ( $T_{air,max}-T_{air,min}$ ).

Aging	opt		15PCM		25PCM		35PCM	
days	LST	Т	LST	Т	LST	Т	LST	Т
	[hh:mm]	$[^{\circ}C]$	[hh:mm]	$[^{\circ}C]$	[hh:mm]	$[^{\circ}C]$	[hh:mm]	$[^{\circ}C]$
0	12:52	41.2	12:27	45.1	12:11	46.0	12:11	46.4
15	12:24	45.3	12:31	48.6	12:13	45.7	12:15	45.2
30	12:38	45.5	12:26	45.7	12:24	45.7	12:10	45.7
60	12:25	48.3	12:31	45.3	12:23	45.3	12:28	48.1

Table 1: Peak temperature value and local standard time at which it was registered in each of the selected membranes, considering different aging periods (0, 15, 30, and 60 days).

timized membrane maintains its temperature above 40 °C for about 3 hours 403 and 52 minutes, while the original material only exceeded this limit for 1 404 hour and 45 minutes. Such an abrupt variation of the optimized membrane 405 performance, allows both the 25PCM and the 35PCM sample to obtain sim-406 ilar thermal performance compared to the OPT sample after 15-days-aging. 407 The 15PCM sample, on the other hand, similarly to the optimized membrane 408 experiences a significant surface temperature increase producing a tempera-409 ture peak of 48.6 °C. 410

After 30 days, all the membranes seem to behave in a similar way and are associated to an almost indistinguishable trend. Finally, after 60-days-aging, the reference membrane with no PCM and the 35PCM solution show the worst thermal response reaching more than 48 °C in the central part of the day.

416

Based on the aforementioned results, we can state that the addition of 417 PCM to the original polyurethane mixture affects the stability of the mem-418 branes thermo-optical performance in time. In order to more carefully inves-419 tigate this phenomenon, we focused our attention on the percentage change 420 in surface temperature, defined as the difference between the surface tem-421 perature of the aged sample  $(T_{aged})$  and the corresponding non-aged one 422  $(T_{non-aged})$ , over the maximum air temperature difference registered in the 423 selected day (T<sub>air,max</sub>-T<sub>air,min</sub>). Figure 9 depicts said variation, grouping the 424 membranes in four different panels (one for each type of membrane), i.e. 425 OPT, 15PCM, 25PCM, and 35PCM. 426

Results demonstrate that the optimized membrane with no PCM addition is associated to the highest variations. In more detail, after 15 days of aging, an average variation by 10.2% is found, while average differences by about



Figure 10: Time spent at temperatures above 40  $^{\circ}$ C for the investigated polyurethane membranes, i.e. (a) OPT-CM, (b) 15PCM-CM, (c) 25PCM-CM, and (d) 35PCM-CM, before the accelerated weathering procedure.

10.9 and 17.6% characterize the membrane after 30 and 60 days of weathering, respectively. Globally, the weathering process causes an abrupt decrease
in the thermo-optic performance of the OPT membrane, which seemed to
stabilize in the medium distance and eventually decrease again after 60 days
of aging.

435

Concerning the PCM-doped membranes, all of them maintain a more 436 stable profile in time. However some variations can be detected among the 437 different types considered in this work. In particular, the use of 25%-in-438 weight of PCM in the selected waterproof application seems to guarantee 439 an acceptable trade-off between reduced deterioration due to thermal expan-440 sion and leakage-induced soiling upon weathering. The 25PCM is, indeed, 441 the only application that allows to obtain a negative average temperature 442 change in all three aging conditions (-0.63, -1.99, and -3.11% after 15, 30, 443 and 60 days, respectively). This particular result suggests that the addition 444 of the selected amount of PCM could represent a further optimization of the 445 innovative cool roof membrane, aimed at improving its long-term durability 446 performance. 447

#### 448 4.3. Comparison between sol-air temperature and radiation-based forcing

Figure 10 shows the comparison among the surface temperature profiles 449 of the four considered membranes exposed to the TaRAD and the Tsol cy-450 cles. As can be seen, the dark-grev-dashed profile, depicting the surface 451 temperature generated by the radiation-based temperature forcing, very well 452 reproduces the shape of the solid red-line trend, representing the thermal 453 behavior of the same membrane exposed to the sol-air temperature-based 454 forcing cycle. However, every graph in Figure 10 shows an average deviation 455 of about 2 °C between the profile produced by the radiation-based temper-456 ature forcing (associated to higher temperatures) and the one from the Tsol 457 cycle (the one that uses the sol air temperature simplification). Said differ-458 ence exceeds the expected experimental error derived from the combination 459 of the acquisition and the environmental forcing system of about 1 °C, and 460 it is probably due to an underestimation of the long-wave radiative exchange 461 with the local environment. 462

Based on this evidence, a specifically designed correction factor could be introduced to take into account the non-negligible effect of the long-wave exchange, at least when horizontal applications are considered. In any case, the radiation-based forcing allowed to reproduce the thermal response of the investigated waterproof-polyurethane-based roofing solutions in a rapid and effective way by exposing all the membranes to the same forcing cycle. The interaction between the short-wave incoming solar radiation and the different surfaces is, in this case, a real physical phenomenon that depends on the specific solar reflectance capability of the investigated membranes.



Figure 11: Comparison between the thermal profiles from the TaRAD and the Tsol cycle for the investigated polyurethane membranes, i.e. (a) OPT-CM, (b) 15PCM-CM, (c) 25PCM-CM, and (d) 35PCM-CM, before the accelerated weathering procedure.

#### 472 5. Conclusions

Building upon previews research aimed at developing an innovative polyurethane
membrane including up to 35%-in-weight of phase change materials with a
melting temperature of 25 °C, this work tackles the thermo-optic durability
of such unique application coupling cool and latent solutions into a composite roofing material for passive cooling purpose.

In more detail, the role of PCMs in improving the cool roof membrane durability when exposed to typical massive thermal fluctuations due to extreme
air temperatures and intense radiation from the sun, was assessed.

481

By shifting from a purely sensible to a partly latent heat storage application, this research aimed to reduce the long-term deterioration of the

membrane due to extreme thermal stresses. In this view, three different roof 484 membranes including organic paraffin in a shape-stabilized solution were de-485 veloped considering 15%, 25%, and 35% of PCM with respect to the weight of 486 the liquid membrane. Additionally, an optimized cool roof membrane includ-487 ing titanium dioxide was also produced for comparison purpose. Said mem-488 branes were later exposed to an accelerated weathering procedure (QUV) for 489 15, 30, and 60 days, according to ASTM D 4329-99 and ASTM G 154-06, 490 and their optic performance was evaluated in terms of reflection coefficient 491 based on ASTM E903-12 before and after the aging procedure. Finally, the 492 thermal performance of all the samples was investigated and compared in 493 terms of roof surface temperature using controlled environmental forcing. In 494 more detail, an ATT DM340SR climatic chamber equipped with a solar sim-495 ulator (halogen lamp) was used to reproduce the local boundary conditions 496 of a typical summer day and expose the samples to a fully controlled and 497 reproducible environmental forcing. The behavior of the membranes was 498 compared using sol-air temperature-based forcing cycles, while the potential 490 use of radiation-based conditioning was assessed and bench-marked to the 500 previous methodology. 501

502

Results showed that the introduction of the latent additive allows to pre-503 serve a more stable solar reflectance capability even after 60 days of ag-504 ing, particularly when 25% in weight of PCM was added to the original 505 polyurethane-based mixture. Concerning the surface temperature monitor-506 ing during controlled environmental forcing, PCM addition to the basic mix-507 ture involved lower thermal performance at time zero, but in the meantime, 508 allowed to maintain a more stable behavior with increasing the weather-509 ing time. In particular, the detrimental temperature increase registered be-510 tween the new and the 15-days-aged OPT sample was significantly reduced 511 by the introduction of the PCM. Additionally, the 25% PCM solution not 512 only maintained its thermo-optic performance, but it actually improved, al-513 though slightly, after 30 and 60 days of aging. As for the radiation-based 514 conditioning, it was shown that though this methodology tends to overstate 515 surface overheating due to the exclusion of the long-wave radiative exchange 516 with the sky, a specifically designed correction factor could be used to rapidly 517 produce reliable temperature profiles. 518

519

In conclusion, the proposed analysis showed how thermal energy storage techniques could be used to improve the thermo-optic durability of waterproof membranes for roofing applications, frequently exposed to severe degradation due to extreme environmental boundary conditions. In particular, the addition of the proper amount of latent storage material could produce a finishing material capable of improving rather then reducing its passive cooling capability after extreme weathering conditions.

#### 527 Acknowledgment

#### 528 Acknowledgment

This research has received funding from the European Union's Horizon 529 2020 research and innovation program under grant agreement n° 657466 530 (INPATH-TES). The authors would like to thank Fondazione cassa di Risparmio 531 di Perugia for supporting the investigation about bio-materials within the 532 project SOS CITTA 2018.0499.026 and Gabriele Franceschetti and CVR 533 s.r.l. company for assisting the development of cool membranes prototypes 534 with integrated PCMs. Cristina Pisellis acknowledgments are due to "Um-535 bria A.R.CO." project of Regione Umbria for supporting her research within 536 the framework of "SMEET-WELL: SMart building management for Energy 537 saving meets WELLbeing" project. 538

#### 539 References

- L. Saikku, A. Rautiainen, P. E. Kauppi, The sustainability challenge of meeting carbon dioxide targets in Europe by 2020, Energy Policy 36 (2) (2008) 730-742. doi:10.1016/j.enpol.2007.10.007.
- [2] N. Soares, J. Bastos, L. Dias Pereira, A. Soares, A. R. Amaral,
  E. Asadi, F. Lamas, E. Rodrigues, H. Monteiro, M. Lopes, A. Gaspar, A review on current advances in the energy and environmental
  performance of buildings towards a more sustainable built environment, Renewable and Sustainable Energy Reviews 77 (2017) 845–860.
  doi:10.1016/j.rser.2017.04.027.
- [3] M. Walls, Energy efficiency: Building labels lead to savings, Nature Energy 1 (2017) 17055. doi:10.1038/nenergy.2017.55.
- [4] F. Ascione, Energy conservation and renewable technologies for build ings to face the impact of the climate change and minimize the use of
   cooling, Solar Energy 154. doi:10.1016/j.solener.2017.01.022.

- <sup>554</sup> [5] D. Jacob, L. Kotova, C. Teichmann, S. Sobolowski, R. Vautard, C. Don<sup>555</sup> nelly, A. Koutroulis, M. Grillakis, I. Tsanis, A. Damm, A. Sakalli, M. van
  <sup>556</sup> Vliet, Climate impacts in Europe under +1.5°C global warming, Earth's
  <sup>557</sup> Futuredoi:10.1002/2017EF000710.
- <sup>558</sup> [6] M. Santamouris, Cooling the buildings past, present and future, Energy and Buildings 128. doi:10.1016/j.enbuild.2016.07.034.
- [7] M. Kaboré, E. Bozonnet, P. Salagnac, M. Abadie, Indexes
  for passive building design in urban context-indoor and outdoor cooling potentials, Energy and Buildings 173 (2018) 315–325.
  doi:10.1016/j.enbuild.2018.05.043.
- [8] H. Akbari, H. D. Matthews, Global cooling updates: Reflective roofs and pavements, Energy and Buildings 55 (2012) 26.
  doi:10.1016/j.enbuild.2012.02.055.
- [9] H. Akbari, C. Cartalis, D. Kolokotsa, A. Muscio, A. L. Pisello,
  F. Rossi, M. Santamouris, A. Synnefa, N. Wong, M. Zinzi, Local climate change and urban heat island mitigation techniques the state of
  the art, Journal of Civil Engineering and Management 22 (2016) 1–16.
  doi:10.3846/13923730.2015.1111934.
- [10] P. Rosado, R. Levinson, Potential benefits of cool walls on residential and commercial buildings across california and the united states: Conserving energy, saving money, and reducing emission of greenhouse gases and air pollutants, Energy and Buildings 199. doi:10.1016/j.enbuild.2019.02.028.
- [11] T. Xu, J. Sathaye, H. Akbari, V. Garg, S. Tetali, Quantifying the direct benefits of cool roofs in an urban setting: Reduced cooling energy use and lowered greenhouse gas emissions, Building and Environment 48 (2012) 1–6. doi:10.1016/j.buildenv.2011.08.011.
- [12] A. H. Rosenfeld, H. Akbari, J. J. Romm, M. Pomerantz, Cool communities: strategies for heat island mitigation and smog reduction, Energy and buildings 28 (1) (1998) 51–62. doi:10.1016/S0378-7788(97)00063-7.
- <sup>584</sup> [13] M. Pomerantz, Are cooler surfaces a cost-effect mitigation of
  <sup>585</sup> urban heat islands?, Urban Climate 24 (2018) 393 397.
  <sup>586</sup> doi:10.1016/j.uclim.2017.04.009.

- [14] C. Piselli, M. Saffari, A. de Gracia, A. L. Pisello, F. Cotana, L. F. Cabeza, Optimization of roof solar reflectance under different climate conditions, occupancy, building configuration and energy systems, Energy and Buildings 151 (2017) 81–97. doi:10.1016/j.enbuild.2017.06.045.
- [15] I. Hernández-Pérez, J. Xamán, E. V. Macías-Melo, K. M. Aguilar-Castro, I. Zavala-Guillén, I. Hernández-López, E. Simá, Experimental thermal evaluation of building roofs with conventional and reflective coatings, Energy and Buildings 158 (2018) 569–579. doi:10.1016/j.enbuild.2017.09.085.
- [16] P. Meenakshi, M. Selvaraj, Bismuth titanate as an infrared reflective pigment for cool roof coating, Solar Energy Materials and Solar Cells 174 (2018) 530–537. doi:10.1016/j.solmat.2017.09.048.
- [17] A. de Gracia, L. F. Cabeza, Phase change materials and thermal energy storage for buildings, Energy and Buildings 88.
  doi:10.1016/j.enbuild.2015.06.007.
- [18] M. Song, F. Niu, N. Mao, Y. Hu, S. Deng, Review on building energy
  performance improvement using phase change materials, Energy and
  Buildings 158 (2018) 776–793. doi:10.1016/j.enbuild.2017.10.066.
- [19] K. Kant, A. Shukla, A. Sharma, Advancement in phase change materials for thermal energy storage applications, Solar Energy Materials and Solar Cells 172 (2017) 82–92. doi:10.1016/j.solmat.2017.07.023.
- [20] L. Calabrese, E. Proverbio, A. Frazzica, V. Brancato, F. Grungo, D. La
  Rosa, V. Palomba, Thermal performance of hybrid cement mortarPCMs for warm climates application, Solar Energy Materials and Solar
  Cells 193 (2019) 270–280. doi:10.1016/j.solmat.2019.01.022.
- [21] H. B. Kim, M. Mae, Y. Choi, T. Kiyota, Experimental analysis of thermal performance in buildings with shape-stabilized
  phase change materials, Energy and Buildings 152 (2017) 524–533.
  doi:10.1016/j.enbuild.2017.07.076.
- [22] M. Genc, Z. Genc, Microencapsulated myristic acidfly ash with tio2 shell
  as a novel phase change material for building application, Journal of
  Thermal Analysis and Calorimetry 131 (2017) 1–8. doi:10.1007/s10973017-6781-7.

- [23] I. Krupa, P. Sobolčiak, H. Abdelrazeq, M. Ouederni, M. A. AlMaadeed, Natural aging of shape stabilized phase change materials based on paraffin wax, Polymer testing 63 (2017) 567–572.
  doi:10.1016/j.polymertesting.2017.09.027.
- [24] Z. Rao, G. Zhang, T. Xu, K. Hong, Experimental study on a novel
  form-stable phase change materials based on diatomite for solar energy storage, Solar Energy Materials and Solar Cells 182 (2018) 52–60.
  doi:10.1016/j.solmat.2018.03.016.
- [25] S. G. Yoon, Y. K. Yang, T. W. Kim, M. H. Chung, J. C. Park, Thermal
   performance test of a phase-change-material cool roof system by a scaled
   model, Advances in Civil Engineering 2018. doi:10.1155/2018/2646103.
- [26] A. Pisello, E. Fortunati, S. Mattioli, L. F. Cabeza, C. Barreneche,
  J. Kenny, F. Cotana, Innovative cool roofing membrane with integrated
  phase change materials: Experimental characterization of morphological, thermal and optic-energy behavior, Energy and Buildings 112 (2016)
  40–48. doi:10.1016/j.enbuild.2015.11.061.
- [27] P. Lassandro, S. Di Turi, Energy efficiency and resilience against increasing temperatures in summer: The use of pcm and cool materials in buildings, International Journal of Heat and Technology 35 (2017)
  S307–S315. doi:10.18280/ijht.35Sp0142.
- [28] Y. K. Yang, I. S. Kang, M. H. Chung, S. Kim, J. C. Park, Effect of pcm cool roof system on the reduction in urban heat island phenomenon, Building and Environment 122 (2017) 411 421. doi:10.1016/j.buildenv.2017.06.015.
- [29] S. Lu, Y. Chen, S. Liu, X. Kong, Experimental research on a novel
  energy efficiency roof coupled with pcm and cool materials, Energy and
  Buildings 127. doi:10.1016/j.enbuild.2016.05.080.
- [30] M. Saffari, C. Piselli, A. de Gracia, A. L. Pisello, F. Cotana, L. F.
  Cabeza, Thermal stress reduction in cool roof membranes using phase
  change materials (pcm), Energy and Buildings 158 (2018) 1097–1105.
  doi:10.1016/j.enbuild.2017.10.068.

- [31] S. Tsoka, T. Theodosiou, K. Tsikaloudaki, F. Flourentzou, Modeling
  the performance of cool pavements and the effect of their aging on outdoor surface and air temperatures, Sustainable Cities and Society 42.
  doi:10.1016/j.scs.2018.07.016.
- [32] M. Sleiman, G. Ban-Weiss, H. E. Gilbert, D. François, P. Berdahl, T. W.
  Kirchstetter, H. Destaillats, R. Levinson, Soiling of building envelope
  surfaces and its effect on solar reflectancepart i: Analysis of roofing
  product databases, Solar Energy Materials and Solar Cells 95 (12) (2011)
  3385–3399. doi:10.1016/j.solmat.2011.08.002.
- [33] M. Sleiman, T. W. Kirchstetter, P. Berdahl, H. E. Gilbert, S. Quelen,
  L. Marlot, C. V. Preble, S. Chen, A. Montalbano, O. Rosseler, et al.,
  Soiling of building envelope surfaces and its effect on solar reflectance–
  part ii: Development of an accelerated aging method for roofing materials, Solar Energy Materials and Solar Cells 122 (2014) 271–281.
  doi:10.1016/j.solmat.2013.11.028.
- [34] M. Sleiman, S. Chen, H. E. Gilbert, T. W. Kirchstetter, P. Berdahl,
  E. Bibian, L. S. Bruckman, D. Cremona, R. H. French, D. A. Gordon, et al., Soiling of building envelope surfaces and its effect on solar reflectance-part iii: Interlaboratory study of an accelerated aging
  method for roofing materials, Solar Energy Materials and Solar Cells
  143 (2015) 581–590. doi:10.1016/j.solmat.2011.08.002.
- [35] C. Ferrari, G. Santunione, A. Libbra, A. Muscio, E. Sgarbi, How accelerated biological aging can affect solar reflective polymeric based building materials, Journal of Physics: Conference Series 923 (2017) 012046.
  doi:10.1088/1742-6596/923/1/012046.
- [36] R. Levinson, P. Berdahl, A. Berhe, H. Akbari, Effect of soiling
  and cleaning on reflectance and solar heat gain of a light-colored
  roofing membrane, Atmospheric Environment 39 (2005) 7807–7824.
  doi:10.1016/j.atmosenv.2005.08.037.
- [37] M. LLC, Cool Roof Rating Council, https://coolroofs.org/, accessed: 2019-10-24.
- 682 [38] N. Alchapar, E. Correa, Aging of roof coatings. solar re-683 flectance stability according to their morphological characteris-

- tics, Construction and Building Materials 102 (2016) 297–305. doi:10.1016/j.conbuildmat.2015.11.005.
- [39] E. Mastrapostoli, M. Santamouris, D. Kolokotsa, P. Vassilis, D. Venieri, K. Gompakis, On the ageing of cool roofs: Measure of the optical degradation, chemical and biological analysis and assessment of the energy impact, Energy and Buildings 114 (2016) 191 199. doi:doi.org/10.1016/j.enbuild.2015.05.030.
- [40] C. Ferrari, A. Gholizadeh Touchaei, M. Sleiman, A. Libbra, A. Muscio,
  C. Siligardi, H. Akbari, Effect of aging processes on solar reflectivity
  of clay roof tiles, Advances in Building Energy Research 8 (1) (2014)
  28–40. doi:10.1080/17512549.2014.890535.
- [41] R. F. De Masi, S. Ruggiero, G. P. Vanoli, Acrylic white paint of industrial sector for cool roofing application: Experimental investigation of summer behavior and aging problem under Mediterranean climate, Solar Energy 169 (2018) 468–487. doi:10.1016/j.solener.2018.05.021.
- [42] T. Aoyama, T. Sonoda, Y. Nakanishi, J. Tanabe, H. Takebayashi, Study on aging of solar reflectance of the self-cleaning
  high reflectance coating, Energy and Buildings 157 (2017) 92–100.
  doi:10.1016/j.enbuild.2017.02.021.
- [43] X. Yang, C. Vang, D. Tallman, G. Bierwagen, S. Croll, S. Rohlik, Weathering degradation of polyurethane coating, Polymer Degradation and
  Stability 74 (2001) 341–351. doi:10.1016/S0141-3910(01)00166-5.
- [44] B. Jelle, Accelerated climate ageing of building materials, components
  and structures in the laboratory, Journal of Materials Science 47 (2012)
  6475–6496. doi:10.1007/s10853-012-6349-7.
- [45] A. L. Pisello, E. Fortunati, C. Fabiani, S. Mattioli, F. Dominici, L. Torre,
  L. F. Cabeza, F. Cotana, Pcm for improving polyurethane-based cool
  roof membranes durability, Solar Energy Materials and Solar Cells 160
  (2017) 34 42. doi:10.1016/j.solmat.2016.09.036.
- [46] G. Santunione, C. Ferrari, C. Siligardi, A. Muscio, E. Sgarbi, Accelerated biological ageing of solar reflective and aesthetically relevant
  building materials, Advances in Building Energy Research (2018) 1–
  18doi:10.1080/17512549.2018.1488616.

- [47] R. Ye, W. Lin, K. Yuan, X. Fang, Z. Zhang, Experimental and numerical investigations on the thermal performance of building plane containing CaCl2·6H2O/expanded graphite composite phase change material, Applied Energy 193 (2017) 325–335. doi:10.1016/j.apenergy.2017.02.049.
- [48] C. Piselli, V. Castaldo, A. L. Pisello, How to enhance thermal energy storage effect of pcm in roofs with varying solar reflectance: Experimental and numerical assessment of a new roof system for passive cooling in different climate conditions, Solar Energydoi:10.1016/j.solener.2018.06.047.
- [49] R. Ricciu, L. A. Besalduch, A. Galatioto, G. Ciulla, Thermal characterization of insulating materials, Renewable and Sustainable Energy Reviews 82 (2016) 1765–1773. doi:10.1016/j.rser.2017.06.057.
- [50] A. D'Alessandro, A. L. Pisello, C. Fabiani, F. Ubertini, L. F. Cabeza,
  F. Cotana, Multifunctional smart concretes with novel phase change
  materials: Mechanical and thermo-energy investigation, Applied Energy
  212 (2018) 1448–1461. doi:10.1016/j.apenergy.2018.01.014.
- [51] M. H. Chung, J. C. Park, Development of PCM cool roof system to control urban heat island considering temperate climatic conditions, Energy
  and Buildings 116 (2016) 341–348. doi:10.1016/j.enbuild.2015.12.056.
- [52] A. L. Pisello, V. Castaldo, G. Pignatta, M. Santamouris, F. Cotana, Experimental in-lab and in-field analysis of waterproof membranes for cool roof application and urban heat island mitigation, Energy and Buildings 114 (2016) 180–190. doi:10.1016/j.enbuild.2015.05.026.
- <sup>740</sup> [53] ASTM D4329-13, Standard practice for fluorescent ultraviolet (uv) lamp
  <sup>741</sup> apparatus exposure of plastics, Standard, ASTM International, West
  <sup>742</sup> Conshohocken, PA (2013). doi:10.1520/D4329-13.
- [54] ASTM G154-06, Standard Practice for Operating Fluorescent Light Apparathus for UV Exposure of Nonmetallic Materials, Standard, ASTM International, West Conshohocken, PA (2006). doi:10.1520/G0154-12A.
- <sup>746</sup> [55] ASTM E903-12, Standard Test Method for Solar Absorptance, Re<sup>747</sup> flectance, and Transmittance of Materials Using Integrating Spheres,
  <sup>748</sup> Standard, ASTM International, West Conshohocken, PA (2012).
  <sup>749</sup> doi:10.1520/E0903-12.

- [56] Angelantoni Test Technologies, http://www.acstestchambers.com/Product/Prodotto?id\_fam=
   (2012).
- [57] ASTM G173-03(2012), Standard tables for reference solar spectral
  irradiances: Direct normal and hemispherical on 37° tilted surface, Standard, ASTM International, West Conshohocken, PA (2012).
  doi:10.1520/G0173-03R12.
- [58] A. V. Sá, M. Azenha, H. De Sousa, A. Samagaio, Thermal enhancement of plastering mortars with phase change materials: Experimental and numerical approach, Energy and Buildings 49 (2012) 1627.
  doi:10.1016/j.enbuild.2012.02.031.
- [59] ISO 6946:2017, Building components and building elements Thermal
   resistance and thermal transmittance Calculation methods, Standard,
   International Organization for Standardization, Geneva, CH (2017).
   URL https://www.iso.org/standard/40968.html
- [60] J. F. Kreider, P. S. Curtiss, A. Rabl, Heating and cooling of buildings:
  design for efficiency, edition, r Edition, Vol. 32, Taylor & Francis Group,
  2013. doi:10.5860/choice.32-1554.
- <sup>767</sup> [61] V. Castaldo, V. Coccia, F. Cotana, G. Pignatta, A. L. Pisello, F. Rossi,
  <sup>768</sup> Thermal-energy analysis of natural "cool" stone aggregates as passive
  <sup>769</sup> cooling and global warming mitigation technique, Urban Climate 14.
  <sup>770</sup> doi:10.1016/j.uclim.2015.05.006.