



UNIVERSITÀ
DEGLI STUDI
FIRENZE

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. Fabiani¹, C. Piselli^{1,2}, A.L. Pisello^{1,2}

¹*CIRIAF - Interuniversity Research Centre, University of Perugia, Italy. Via G. Duranti 63 06125 Perugia (Italy)*

²*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,

1 **1. Introduction**

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

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

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

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

69 De Masi et al. [41] found, through in-field test, that the solar reflectance
70 of an acrylic white paint for cool roof applications can decrease from 0.67 to
71 0.48 after 1 year of exposure to the outdoor environment. Similarly, Aoyama
72 et al. [42] demonstrated the increased durability due to the self-cleaning

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

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

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

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

122 **2. Materials and sample preparation**

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

135
136 The prototype membranes were produced by simply mixing the solid-state
137 non-encapsulated paraffin within the membrane tank with liquid polyurethane,
138 while keeping an ambient temperature of $20 \text{ }^\circ\text{C}$ to prevent the PCM from
139 melting during this phase. In the previous works, three different specimens
140 were produced, i.e. a reference “pure-cool” membrane with no additives
141 (noOPT), a cool membrane with “optimized-cool” surface (OPT) and three
142 cool membranes with 15%, 25%, and 35% in weight of PCM added to the
143 original mix design with titanium dioxide and the micro-spheres, i.e. 15PCM,
144 25PCM and 35PCM, respectively (see Figure 1).

145

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

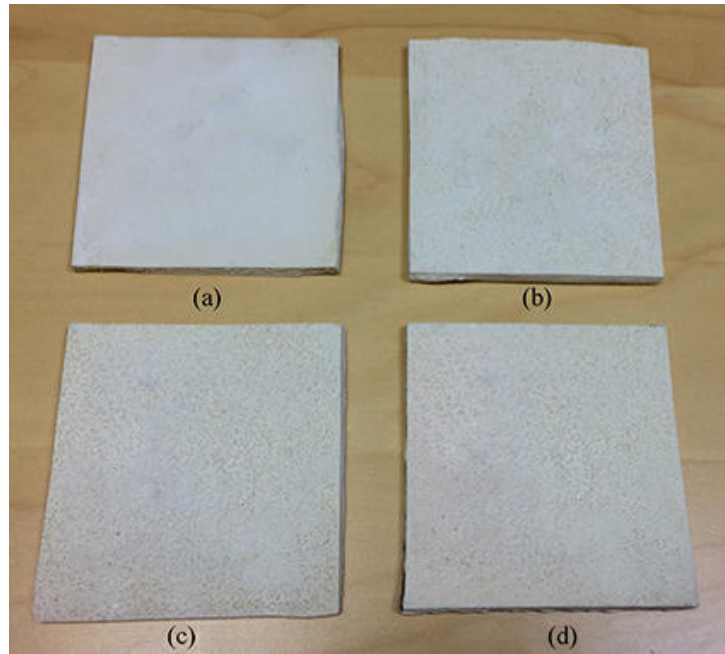


Figure 1: Investigated polyurethane membranes: (a) OPT, (b) 15PCM, (c) 25PCM, and (d) 35PCM, before the accelerated weathering procedure.

152 **3. Experimental methodology**

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

- 155 - development of the proposed cool roof solution through the integration
156 of an organic PCM, i.e. paraffin-based material, into the polyurethane-
157 based cool membrane in different percentages [52, 26];
- 158 - accelerated weathering procedure of the different membranes according
159 to ASTM D 4329-99 (Standard Practice for Fluorescent Ultraviolet

- 160 (UV) Lamp Apparatus Exposure of Plastics) [53] and ASTM G154 -
 161 06 (Standard Practice for Operating Fluorescent Light Apparatus for
 162 UV Exposure of Nonmetallic Materials) [54];
- 163 - surface characterization of the membranes in terms of spectral near
 164 normal-hemispherical reflectance according to ASTM E903-12 (Stan-
 165 dard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres) [55];
 166
 - 167 - thermal characterization of the membranes at different aging times, i.e.
 168 non-aged, 15, 30, and 60 days of aging using the sol-air temperature
 169 ($T_{\text{Sol-air}}$);
 - 170 - thermal characterization of the non-aged membranes using a halogen
 171 UV-lamp and comparison with the profiles from the sol-air temperature
 172 ($T_{\text{Sol-air}}$) analysis.



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

173 3.1. Accelerated weathering test

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

- 179 - 8 hours of UVA radiation (340 nm, energy of $0.77 \text{ W}\cdot\text{m}^{-2}$) at $50 \text{ }^\circ\text{C}$;
- 180 - 2 hours in humid condition (100 RH%) at $40 \text{ }^\circ\text{C}$;
- 181 - 2 hours in humid condition (100 RH%) at $20 \text{ }^\circ\text{C}$.

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

190
191 The effect of the accelerated weathering test on the different samples of
192 cool membranes was evaluated after 15, 30, and 60 days of exposure, based
193 on the common practice derived from the two reference ASTM standards
194 [53, 54]. More in detail, three samples per type were exposed to the test.
195 The first series of samples, one for each type (OPT, 15PCM, 25PCM, and
196 35PCM), was extracted out of the machine after 15 days, the second series
197 was extracted after 30 days, and the last series was extracted after 60 days.

198 *3.2. Spectral near normal-hemispherical reflectance*

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

207 *3.3. Thermal monitoring in real dynamic conditions*

208 The thermal characterization of the membranes was carried in two differ-
209 ent stages. First, each membrane was exposed to a hygro-thermal condition-
210 ing cycle using the sol-air temperature. Secondly, the non-aged samples were
211 exposed to an additional hygro-thermal forcing procedure, making use of a

212 solar simulator to reproduce the incoming radiative flux. The former proce-
213 dure was aimed at evaluating the differential response of the membranes after
214 different aging times; the latter, at comparing the thermal profiles produced
215 using the sol-air temperature (defined in more details in the following) with
216 the ones registered using the solar simulator.

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

226

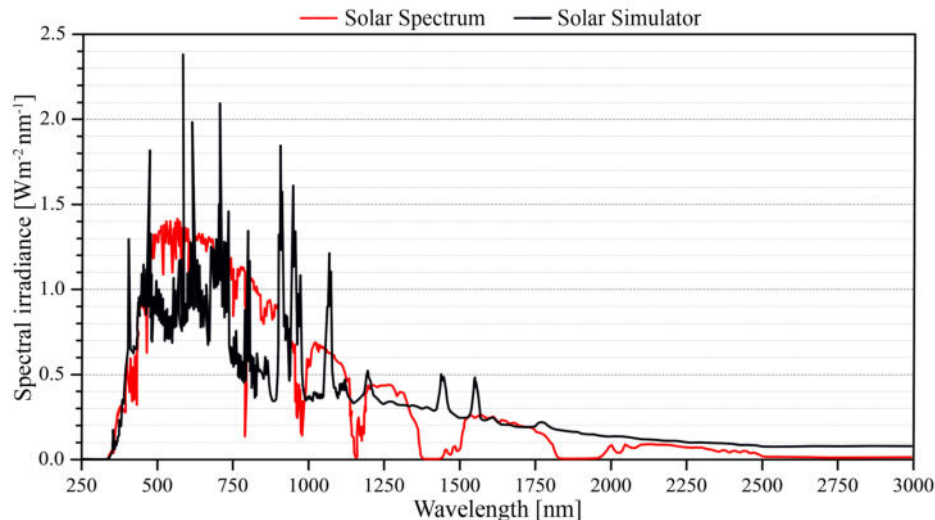


Figure 3: Spectrum of the solar simulator (halogen lamp) compared to the AM 1.5 direct solar spectrum from ASTM G173–03(2012) (Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface) [57].

227 During the experimental campaign, each type of membrane was housed
228 within the controlled environment of the climatic chamber, and exposed to
229 specifically designed environmental cycles. More in detail, real meteorological
230 data from a weather station located on the rooftop of a University building

231 located in central Italy (Perugia) were used to investigate the effect of the
232 selected phase change materials on the long-term durability of the advanced
233 cool roof membranes. In particular, weather data from a typical hot summer
234 day, i.e. 2017-07-26, were selected to be reproduced within the simulated
235 environment of the climatic chamber (see Figure 5).

236

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

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

252

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

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

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

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

$$T_{\text{Sol-air}} = T_{\text{air}} + \alpha I_g R_{\text{se}} - \Delta Q_{\text{ir}} R_{\text{se}} \quad (1)$$

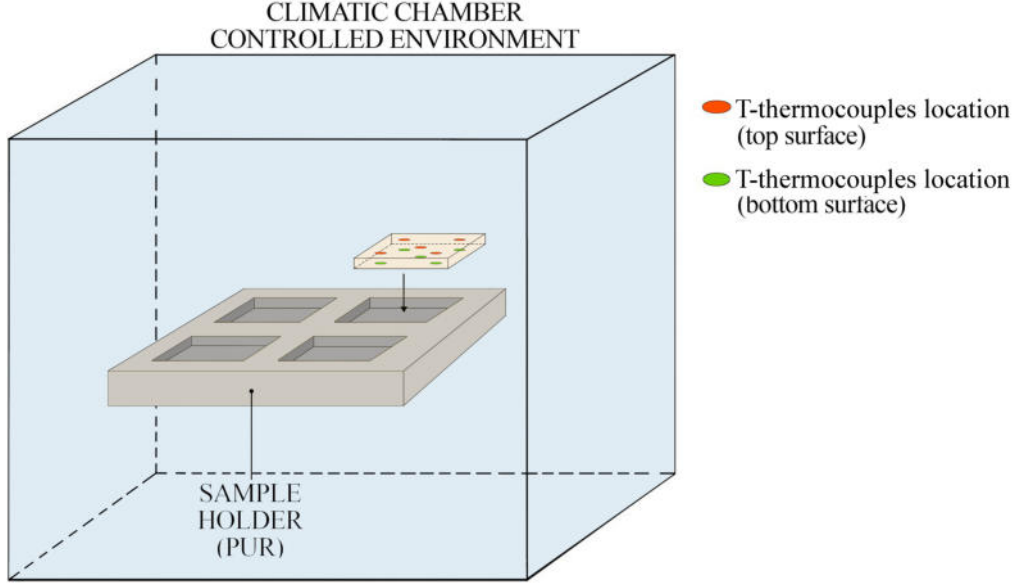


Figure 4: Schematic representation of the experimental setup.

265 where T_{air} is the outdoor air temperature from the weather file ($^{\circ}\text{C}$); α is
 266 the solar absorptance of the specific membranes; I_g is the global solar radi-
 267 ation from the weather file ($\text{W}\cdot\text{m}^{-2}$); R_{se} is the external surface resistance
 268 ($\text{m}^2\cdot(\text{K}\cdot\text{W})^{-1}$); and ΔQ_{ir} is the correction to infrared radiation transfer be-
 269 tween surface and environment if sky temperature is different from T_{air} ,
 270 ($\text{W}\cdot\text{m}^{-2}$).

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

277

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

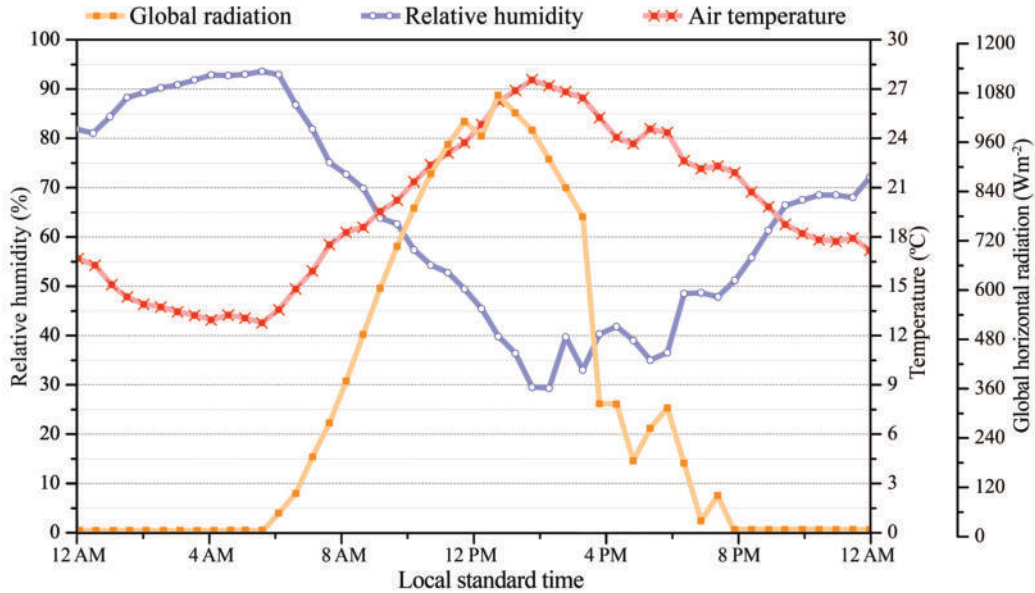


Figure 5: Relative humidity, air temperature, and global radiation (in the range 300 – 2800 nm) values registered by the weather station at Perugia University on July 26, 2017.

283 values presented in Section 4.1.

284 3.3.2. Radiation-based cycles

285 At a later stage, the non-aged membranes were exposed to an additional
 286 environmental cycle (the air temperature-radiation based – TaRAD – cycle),
 287 which was designed to exactly reproduce the local climatic conditions in
 288 terms of outdoor air temperature, relative humidity, and global radiation
 289 flux on the horizontal surface from 7:30 AM to 5:30 PM (LST). This specific
 290 time range was selected due to technical limitations: the solar simulator only
 291 allows to reproduce radiative fluxes above $250 \text{ W}\cdot\text{m}^{-2}$.

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

300

301 All this considered, using solar simulators could significantly reduce ex-
302 perimental time. However, solar simulator are often associated to non-
303 negligible deviations in terms of short-wave radiation accuracy, and lack of
304 long-wave radiative exchange with the sky. In this view, the main purpose of
305 this analysis is to compare the thermal profiles produced using sol-air tem-
306 peratures with the ones registered using the solar simulator and evaluate the
307 actual deviation between these conditioning techniques.

308 4. Results and discussions

309 4.1. Thermo-optic performance of the roof membranes

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

323 As a consequence, larger shadows are produced and lower reflectances are
324 obtained with increasing PCM percentages [61]. Said reduction is particu-
325 larly large in the case of the 35PCM sample, which reaches a reflectance of
326 0.51, before aging.

327

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

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

341 Concerning the 25% PCM-doped solution, this particular PCM concen-
342 tration shows the most promising long-term performance. The slope of the
343 25PCM fitting line, indeed, tends to zero in this case.

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

348

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

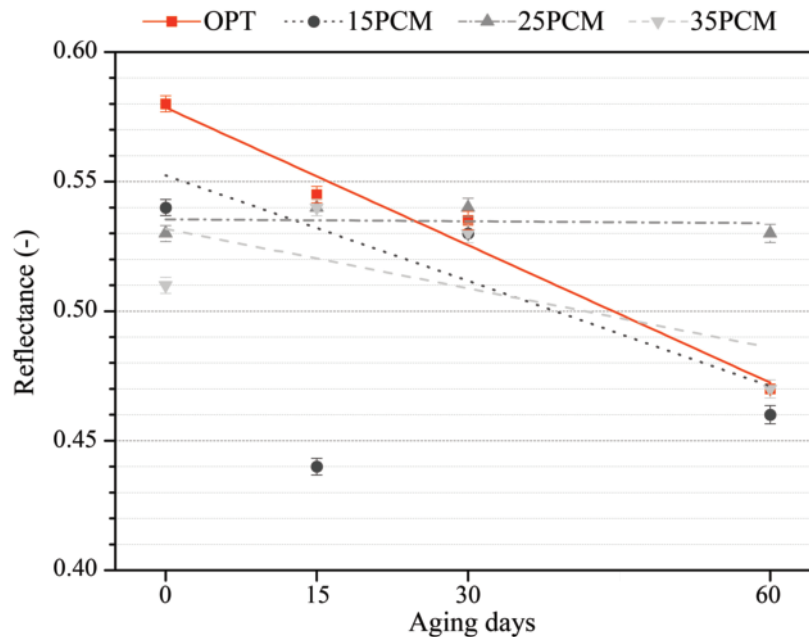


Figure 6: Total solar reflectance for the investigated polyurethane membranes, i.e. OPT-CM, 15PCM-CM, 25PCM-CM, and 35PCM-CM, before and after the accelerated weathering procedure.

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

361
362 The introduction of PCMs, being capable to store part of the heat in
363 the latent form, is expected to reduce such temperature gradients and the
364 albedo degradation with it. However, only the 25PCM sample maintains a
365 higher reflectance throughout the aging. This suggests that PCM concentra-
366 tions around 15% and 35% do not allow the latent additive to fulfill its buffer
367 task. In particular, it seems that lower PCM concentrations do not guarantee
368 enough energy density to overcome the detrimental mechanical deterioration
369 of the substrate, which consequently experiences a similar thermally-driven
370 micro-cracking process. Therefore, as experienced by a direct visual and tac-
371 tile inspection, the liquid PCM leaks out of the membrane already after 15
372 days aging, reducing its surface reflectance.

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

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

383 *4.2. Effect of phase change materials on the surface temperature of the aged* 384 *cool roof membranes*

385 Figure 8 shows the comparison among different surface temperature pro-
386 files monitored during the imposed T_{sol} cycles for each kind of membrane
387 and weathering time. In particular, profiles with the same QUV exposure
388 time are grouped and plotted on the same panel, allowing us to compare

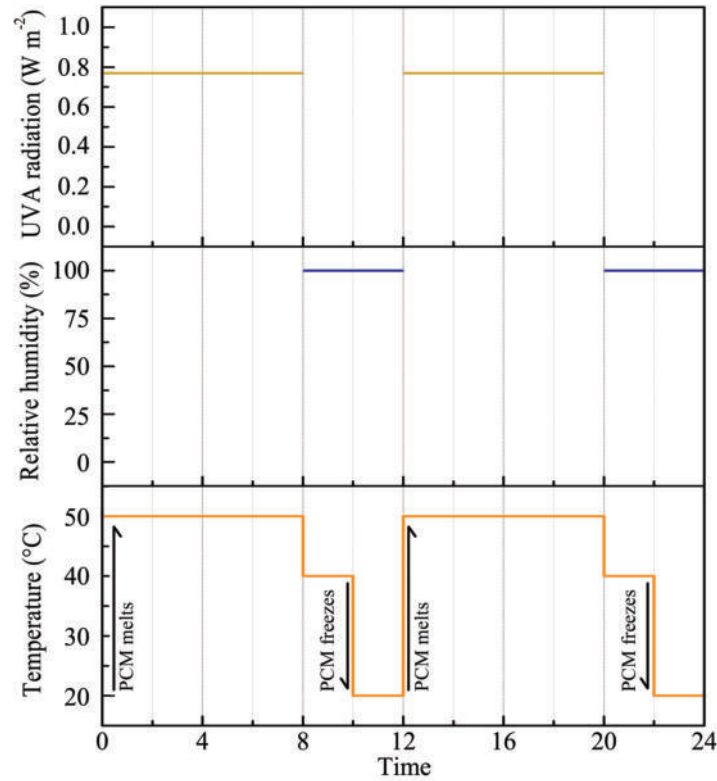


Figure 7: Forcing profiles for a typical QUV aging day.

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

391 As expected, at time zero the TiO₂-optimized membrane with no PCM
 392 addition produces the lowest surface temperature profile, exceeding 40 °C
 393 only in the central part of the day (between 11:45 AM and 1:27 PM (LST),
 394 as shown in Figure 10 and Table 1). Concerning the three considered PCM-
 395 doped solutions, according to the previously described solar reflectances, an
 396 increased temperature trend is produced when increasing the weight percent-
 397 age of the latent additive in the roofing membrane. However, no significant
 398 difference can be seen between the 25 and the 35% PCM solution. After 15
 399 days of accelerated weathering, the reference optimized membrane with no
 400 PCM suffers by a non-negligible temperature increase, featuring a wider tem-
 401 perature bell with a peak value of 45.3 °C versus the 41.2 °C registered before
 402 the aging process. Additionally, Figure 10 shows that the 15-days-aged op-

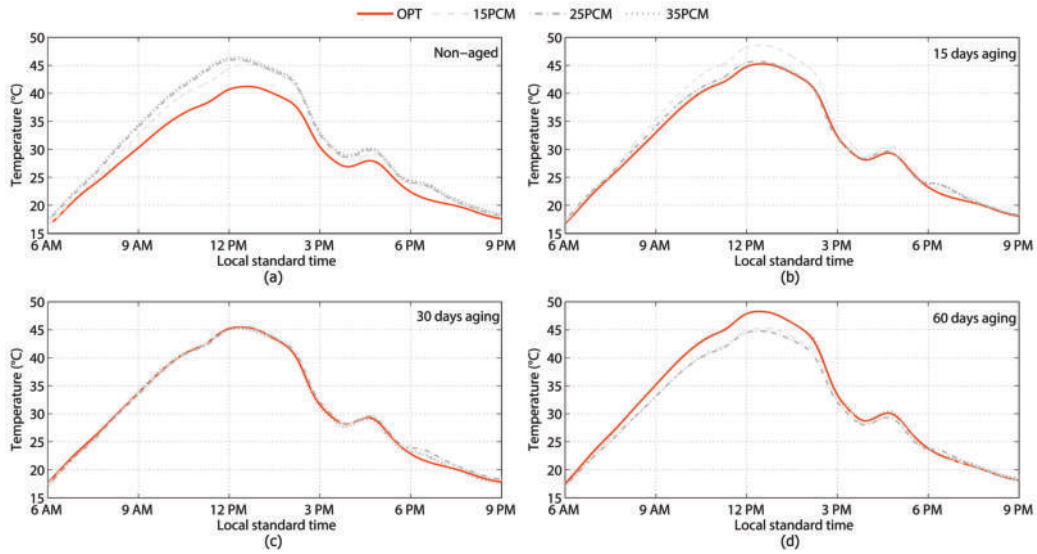


Figure 8: Comparison among the different superficial temperature profiles from the T_{sol} cycles considering the same accelerated weathering time, i.e. (a) 0 days, (b) 15 days, (c) 30 days, (d) 60 days.

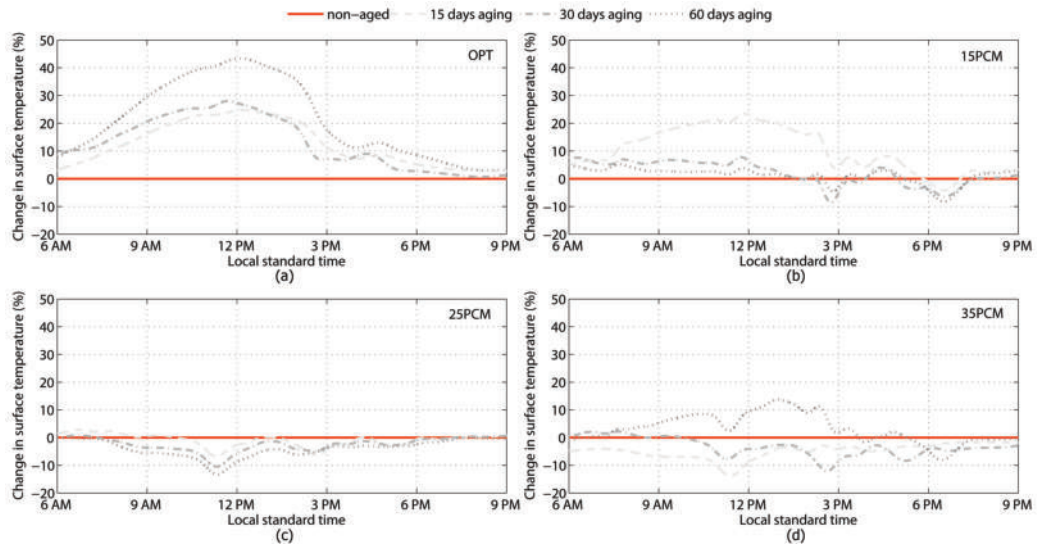


Figure 9: Change in surface temperature of the considered membranes, i.e. (a) OPT, (b) 15PCM, (c) 25PCM, (d) 35PCM, when exposed to 15, 30, and 60 days of accelerated weathering procedure with respect to the maximum air temperature difference registered in the selected day $(T_{aged} - T_{non-aged})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

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).

Aging days	opt		15PCM		25PCM		35PCM	
	LST [hh:mm]	T [°C]	LST [hh:mm]	T [°C]	LST [hh:mm]	T [°C]	LST [hh:mm]	T [°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

403 timized membrane maintains its temperature above 40 °C for about 3 hours
 404 and 52 minutes, while the original material only exceeded this limit for 1
 405 hour and 45 minutes. Such an abrupt variation of the optimized membrane
 406 performance, allows both the 25PCM and the 35PCM sample to obtain sim-
 407 ilar thermal performance compared to the OPT sample after 15-days-aging.
 408 The 15PCM sample, on the other hand, similarly to the optimized membrane
 409 experiences a significant surface temperature increase producing a tempera-
 410 ture peak of 48.6 °C.
 411 After 30 days, all the membranes seem to behave in a similar way and are
 412 associated to an almost indistinguishable trend. Finally, after 60-days-aging,
 413 the reference membrane with no PCM and the 35PCM solution show the
 414 worst thermal response reaching more than 48 °C in the central part of the
 415 day.

416
 417 Based on the aforementioned results, we can state that the addition of
 418 PCM to the original polyurethane mixture affects the stability of the mem-
 419 branes thermo-optical performance in time. In order to more carefully inves-
 420 tigate this phenomenon, we focused our attention on the percentage change
 421 in surface temperature, defined as the difference between the surface tem-
 422 perature of the aged sample (T_{aged}) and the corresponding non-aged one
 423 ($T_{\text{non-aged}}$), over the maximum air temperature difference registered in the
 424 selected day ($T_{\text{air,max}} - T_{\text{air,min}}$). Figure 9 depicts said variation, grouping the
 425 membranes in four different panels (one for each type of membrane), i.e.
 426 OPT, 15PCM, 25PCM, and 35PCM.

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

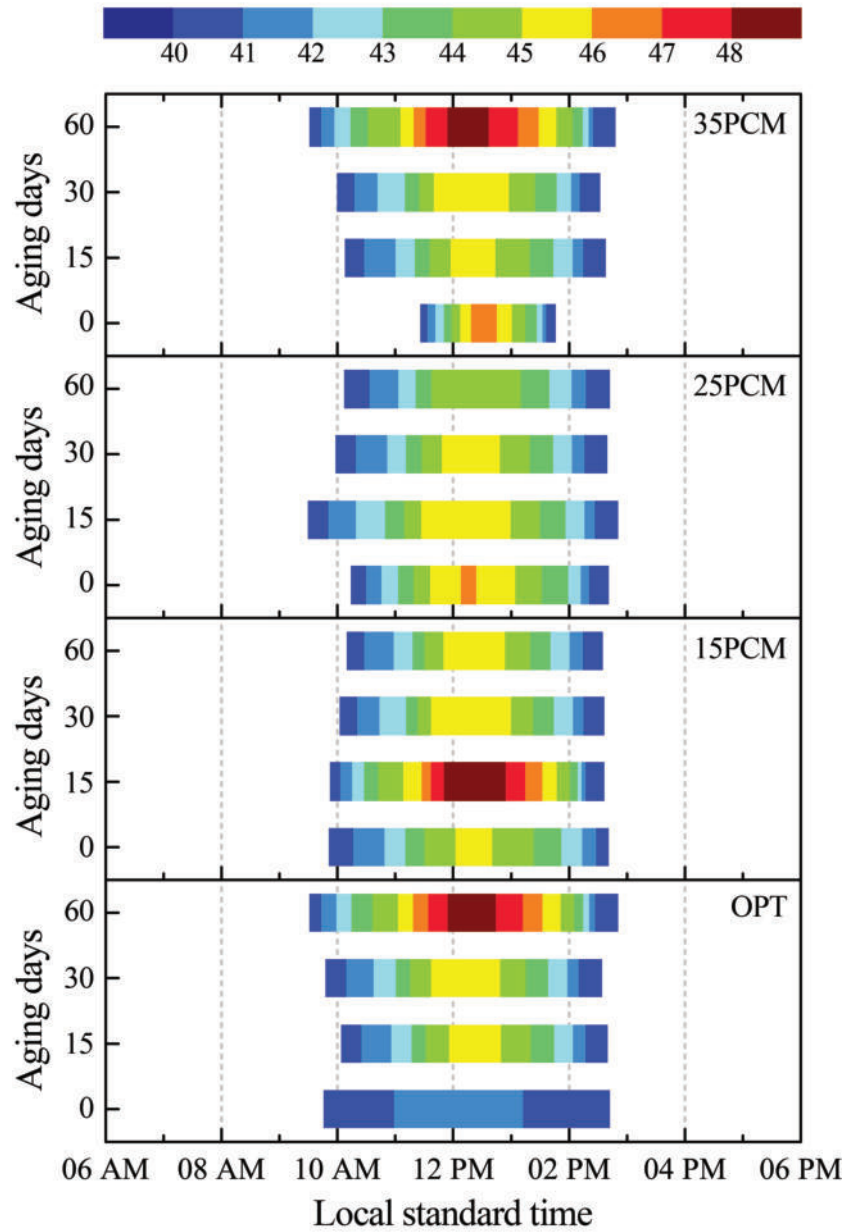


Figure 10: Time spent at temperatures above 40 °C for the investigated polyurethane membranes, i.e. (a) OPT-CM, (b) 15PCM-CM, (c) 25PCM-CM, and (d) 35PCM-CM, before the accelerated weathering procedure.

430 10.9 and 17.6% characterize the membrane after 30 and 60 days of weather-
431 ing, respectively. Globally, the weathering process causes an abrupt decrease
432 in the thermo-optic performance of the OPT membrane, which seemed to
433 stabilize in the medium distance and eventually decrease again after 60 days
434 of aging.

435

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

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

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

463 Based on this evidence, a specifically designed correction factor could be
464 introduced to take into account the non-negligible effect of the long-wave
465 exchange, at least when horizontal applications are considered. In any case,
466 the radiation-based forcing allowed to reproduce the thermal response of

467 the investigated waterproof-polyurethane-based roofing solutions in a rapid
 468 and effective way by exposing all the membranes to the same forcing cycle.
 469 The interaction between the short-wave incoming solar radiation and the
 470 different surfaces is, in this case, a real physical phenomenon that depends
 471 on the specific solar reflectance capability of the investigated membranes.

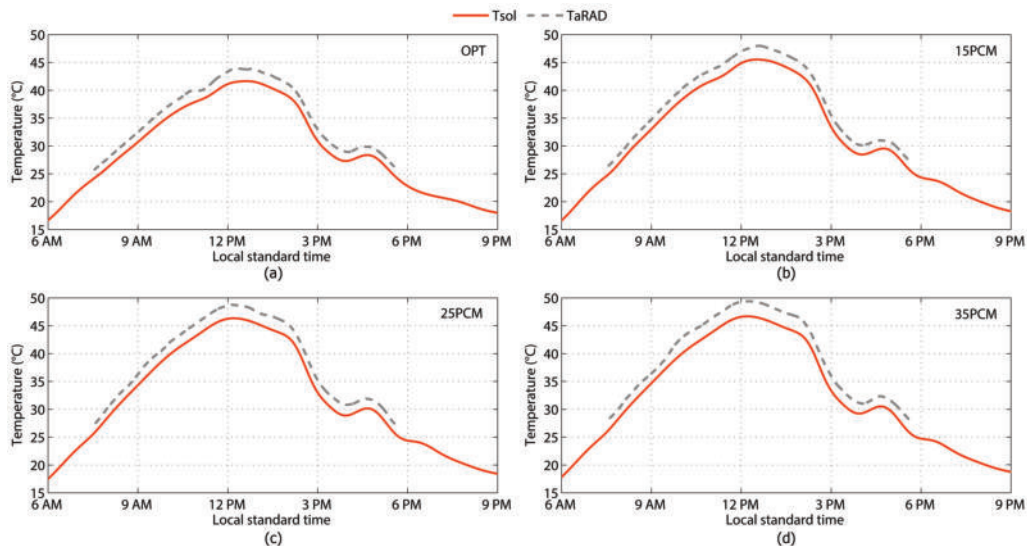


Figure 11: Comparison between the thermal profiles from the TaRAD and the Tsol cycle for the investigated polyurethane membranes, i.e. (a) OPT-CM, (b) 15PCM-CM, (c) 25PCM-CM, and (d) 35PCM-CM, before the accelerated weathering procedure.

472 5. Conclusions

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

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

481

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

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

502
503 Results showed that the introduction of the latent additive allows to pre-
504 serve a more stable solar reflectance capability even after 60 days of ag-
505 ing, particularly when 25% in weight of PCM was added to the original
506 polyurethane-based mixture. Concerning the surface temperature monitor-
507 ing during controlled environmental forcing, PCM addition to the basic mix-
508 ture involved lower thermal performance at time zero, but in the meantime,
509 allowed to maintain a more stable behavior with increasing the weather-
510 ing time. In particular, the detrimental temperature increase registered be-
511 tween the new and the 15-days-aged OPT sample was significantly reduced
512 by the introduction of the PCM. Additionally, the 25% PCM solution not
513 only maintained its thermo-optic performance, but it actually improved, al-
514 though slightly, after 30 and 60 days of aging. As for the radiation-based
515 conditioning, it was shown that though this methodology tends to overstate
516 surface overheating due to the exclusion of the long-wave radiative exchange
517 with the sky, a specifically designed correction factor could be used to rapidly
518 produce reliable temperature profiles.

519
520 In conclusion, the proposed analysis showed how thermal energy storage
521 techniques could be used to improve the thermo-optic durability of water-

522 proof membranes for roofing applications, frequently exposed to severe degra-
523 dation due to extreme environmental boundary conditions. In particular, the
524 addition of the proper amount of latent storage material could produce a fin-
525 ishing material capable of improving rather than reducing its passive cooling
526 capability after extreme weathering conditions.

527 **Acknowledgment**

528 **Acknowledgment**

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

539 **References**

- 540 [1] L. Saikku, A. Rautiainen, P. E. Kauppi, The sustainability challenge of
541 meeting carbon dioxide targets in Europe by 2020, *Energy Policy* 36 (2)
542 (2008) 730–742. doi:10.1016/j.enpol.2007.10.007.
- 543 [2] N. Soares, J. Bastos, L. Dias Pereira, A. Soares, A. R. Amaral,
544 E. Asadi, F. Lamas, E. Rodrigues, H. Monteiro, M. Lopes, A. Gas-
545 par, A review on current advances in the energy and environmental
546 performance of buildings towards a more sustainable built environ-
547 ment, *Renewable and Sustainable Energy Reviews* 77 (2017) 845–860.
548 doi:10.1016/j.rser.2017.04.027.
- 549 [3] M. Walls, Energy efficiency: Building labels lead to savings, *Nature*
550 *Energy* 1 (2017) 17055. doi:10.1038/nenergy.2017.55.
- 551 [4] F. Ascione, Energy conservation and renewable technologies for build-
552 ings to face the impact of the climate change and minimize the use of
553 cooling, *Solar Energy* 154. doi:10.1016/j.solener.2017.01.022.

- 554 [5] D. Jacob, L. Kotova, C. Teichmann, S. Sobolowski, R. Vautard, C. Don-
555 nelly, A. Koutroulis, M. Grillakis, I. Tsanis, A. Damm, A. Sakalli, M. van
556 Vliet, Climate impacts in Europe under +1.5°C global warming, *Earth's*
557 *Future* doi:10.1002/2017EF000710.
- 558 [6] M. Santamouris, Cooling the buildings past, present and future, *Energy*
559 *and Buildings* 128. doi:10.1016/j.enbuild.2016.07.034.
- 560 [7] M. Kaboré, E. Bozonnet, P. Salagnac, M. Abadie, Indexes
561 for passive building design in urban context—indoor and out-
562 door cooling potentials, *Energy and Buildings* 173 (2018) 315–325.
563 doi:10.1016/j.enbuild.2018.05.043.
- 564 [8] H. Akbari, H. D. Matthews, Global cooling updates: Reflec-
565 tive roofs and pavements, *Energy and Buildings* 55 (2012) 26.
566 doi:10.1016/j.enbuild.2012.02.055.
- 567 [9] H. Akbari, C. Cartalis, D. Kolokotsa, A. Muscio, A. L. Pisello,
568 F. Rossi, M. Santamouris, A. Synnefa, N. Wong, M. Zinzi, Local cli-
569 mate change and urban heat island mitigation techniques - the state of
570 the art, *Journal of Civil Engineering and Management* 22 (2016) 1–16.
571 doi:10.3846/13923730.2015.1111934.
- 572 [10] P. Rosado, R. Levinson, Potential benefits of cool walls on resi-
573 dential and commercial buildings across california and the united
574 states: Conserving energy, saving money, and reducing emission
575 of greenhouse gases and air pollutants, *Energy and Buildings* 199.
576 doi:10.1016/j.enbuild.2019.02.028.
- 577 [11] T. Xu, J. Sathaye, H. Akbari, V. Garg, S. Tetali, Quantifying the direct
578 benefits of cool roofs in an urban setting: Reduced cooling energy use
579 and lowered greenhouse gas emissions, *Building and Environment* 48
580 (2012) 1–6. doi:10.1016/j.buildenv.2011.08.011.
- 581 [12] A. H. Rosenfeld, H. Akbari, J. J. Romm, M. Pomerantz, Cool commu-
582 nities: strategies for heat island mitigation and smog reduction, *Energy*
583 *and buildings* 28 (1) (1998) 51–62. doi:10.1016/S0378-7788(97)00063-7.
- 584 [13] M. Pomerantz, Are cooler surfaces a cost-effect mitigation of
585 urban heat islands?, *Urban Climate* 24 (2018) 393 – 397.
586 doi:10.1016/j.uclim.2017.04.009.

- 587 [14] C. Piselli, M. Saffari, A. de Gracia, A. L. Pisello, F. Cotana, L. F.
588 Cabeza, Optimization of roof solar reflectance under different climate
589 conditions, occupancy, building configuration and energy systems, *En-
590 ergy and Buildings* 151 (2017) 81–97. doi:10.1016/j.enbuild.2017.06.045.
- 591 [15] I. Hernández-Pérez, J. Xamán, E. V. Macías-Melo, K. M. Aguilar-
592 Castro, I. Zavala-Guillén, I. Hernández-López, E. Simá, Exper-
593 imental thermal evaluation of building roofs with conventional
594 and reflective coatings, *Energy and Buildings* 158 (2018) 569–579.
595 doi:10.1016/j.enbuild.2017.09.085.
- 596 [16] P. Meenakshi, M. Selvaraj, Bismuth titanate as an infrared reflective
597 pigment for cool roof coating, *Solar Energy Materials and Solar Cells*
598 174 (2018) 530–537. doi:10.1016/j.solmat.2017.09.048.
- 599 [17] A. de Gracia, L. F. Cabeza, Phase change materials and ther-
600 mal energy storage for buildings, *Energy and Buildings* 88.
601 doi:10.1016/j.enbuild.2015.06.007.
- 602 [18] M. Song, F. Niu, N. Mao, Y. Hu, S. Deng, Review on building energy
603 performance improvement using phase change materials, *Energy and*
604 *Buildings* 158 (2018) 776–793. doi:10.1016/j.enbuild.2017.10.066.
- 605 [19] K. Kant, A. Shukla, A. Sharma, Advancement in phase change materi-
606 als for thermal energy storage applications, *Solar Energy Materials and*
607 *Solar Cells* 172 (2017) 82–92. doi:10.1016/j.solmat.2017.07.023.
- 608 [20] L. Calabrese, E. Proverbio, A. Frazzica, V. Brancato, F. Grungo, D. La
609 Rosa, V. Palomba, Thermal performance of hybrid cement mortar-
610 PCMs for warm climates application, *Solar Energy Materials and Solar*
611 *Cells* 193 (2019) 270–280. doi:10.1016/j.solmat.2019.01.022.
- 612 [21] H. B. Kim, M. Mae, Y. Choi, T. Kiyota, Experimental anal-
613 ysis of thermal performance in buildings with shape-stabilized
614 phase change materials, *Energy and Buildings* 152 (2017) 524–533.
615 doi:10.1016/j.enbuild.2017.07.076.
- 616 [22] M. Genc, Z. Genc, Microencapsulated myristic acidfly ash with tio2 shell
617 as a novel phase change material for building application, *Journal of*
618 *Thermal Analysis and Calorimetry* 131 (2017) 1–8. doi:10.1007/s10973-
619 017-6781-7.

- 620 [23] I. Krupa, P. Sobolčiak, H. Abdelrazeq, M. Ouederni, M. A. Al-
621 Maadeed, Natural aging of shape stabilized phase change mate-
622 rials based on paraffin wax, *Polymer testing* 63 (2017) 567–572.
623 doi:10.1016/j.polymertesting.2017.09.027.
- 624 [24] Z. Rao, G. Zhang, T. Xu, K. Hong, Experimental study on a novel
625 form-stable phase change materials based on diatomite for solar en-
626 ergy storage, *Solar Energy Materials and Solar Cells* 182 (2018) 52–60.
627 doi:10.1016/j.solmat.2018.03.016.
- 628 [25] S. G. Yoon, Y. K. Yang, T. W. Kim, M. H. Chung, J. C. Park, Thermal
629 performance test of a phase-change-material cool roof system by a scaled
630 model, *Advances in Civil Engineering* 2018. doi:10.1155/2018/2646103.
- 631 [26] A. Pisello, E. Fortunati, S. Mattioli, L. F. Cabeza, C. Barreneche,
632 J. Kenny, F. Cotana, Innovative cool roofing membrane with integrated
633 phase change materials: Experimental characterization of morphologi-
634 cal, thermal and optic-energy behavior, *Energy and Buildings* 112 (2016)
635 40–48. doi:10.1016/j.enbuild.2015.11.061.
- 636 [27] P. Lassandro, S. Di Turi, Energy efficiency and resilience against in-
637 creasing temperatures in summer: The use of pcm and cool materials
638 in buildings, *International Journal of Heat and Technology* 35 (2017)
639 S307–S315. doi:10.18280/ijht.35Sp0142.
- 640 [28] Y. K. Yang, I. S. Kang, M. H. Chung, S. Kim, J. C. Park, Ef-
641 fect of pcm cool roof system on the reduction in urban heat is-
642 land phenomenon, *Building and Environment* 122 (2017) 411 – 421.
643 doi:10.1016/j.buildenv.2017.06.015.
- 644 [29] S. Lu, Y. Chen, S. Liu, X. Kong, Experimental research on a novel
645 energy efficiency roof coupled with pcm and cool materials, *Energy and*
646 *Buildings* 127. doi:10.1016/j.enbuild.2016.05.080.
- 647 [30] M. Saffari, C. Piselli, A. de Gracia, A. L. Pisello, F. Cotana, L. F.
648 Cabeza, Thermal stress reduction in cool roof membranes using phase
649 change materials (pcm), *Energy and Buildings* 158 (2018) 1097–1105.
650 doi:10.1016/j.enbuild.2017.10.068.

- 651 [31] S. Tsoka, T. Theodosiou, K. Tsikaloudaki, F. Flourentzou, Modeling
652 the performance of cool pavements and the effect of their aging on out-
653 door surface and air temperatures, *Sustainable Cities and Society* 42.
654 doi:10.1016/j.scs.2018.07.016.
- 655 [32] M. Sleiman, G. Ban-Weiss, H. E. Gilbert, D. François, P. Berdahl, T. W.
656 Kirchstetter, H. Destailats, R. Levinson, Soiling of building envelope
657 surfaces and its effect on solar reflectancepart i: Analysis of roofing
658 product databases, *Solar Energy Materials and Solar Cells* 95 (12) (2011)
659 3385–3399. doi:10.1016/j.solmat.2011.08.002.
- 660 [33] M. Sleiman, T. W. Kirchstetter, P. Berdahl, H. E. Gilbert, S. Quelen,
661 L. Marlot, C. V. Preble, S. Chen, A. Montalbano, O. Rosseler, et al.,
662 Soiling of building envelope surfaces and its effect on solar reflectance–
663 part ii: Development of an accelerated aging method for roofing ma-
664 terials, *Solar Energy Materials and Solar Cells* 122 (2014) 271–281.
665 doi:10.1016/j.solmat.2013.11.028.
- 666 [34] M. Sleiman, S. Chen, H. E. Gilbert, T. W. Kirchstetter, P. Berdahl,
667 E. Bibian, L. S. Bruckman, D. Cremona, R. H. French, D. A. Gor-
668 don, et al., Soiling of building envelope surfaces and its effect on so-
669 lar reflectance–part iii: Interlaboratory study of an accelerated aging
670 method for roofing materials, *Solar Energy Materials and Solar Cells*
671 143 (2015) 581–590. doi:10.1016/j.solmat.2011.08.002.
- 672 [35] C. Ferrari, G. Santunione, A. Libbra, A. Muscio, E. Sgarbi, How accel-
673 erated biological aging can affect solar reflective polymeric based build-
674 ing materials, *Journal of Physics: Conference Series* 923 (2017) 012046.
675 doi:10.1088/1742-6596/923/1/012046.
- 676 [36] R. Levinson, P. Berdahl, A. Berhe, H. Akbari, Effect of soiling
677 and cleaning on reflectance and solar heat gain of a light-colored
678 roofing membrane, *Atmospheric Environment* 39 (2005) 7807–7824.
679 doi:10.1016/j.atmosenv.2005.08.037.
- 680 [37] M. LLC, Cool Roof Rating Council, <https://coolroofs.org/>, ac-
681 cessed: 2019-10-24.
- 682 [38] N. Alchapar, E. Correa, Aging of roof coatings. solar re-
683 flectance stability according to their morphological characteris-

- 684 tics, *Construction and Building Materials* 102 (2016) 297–305.
685 doi:10.1016/j.conbuildmat.2015.11.005.
- 686 [39] E. Mastrapostoli, M. Santamouris, D. Kolokotsa, P. Vassilis, D. Ve-
687 nieri, K. Gompakis, On the ageing of cool roofs: Measure of the
688 optical degradation, chemical and biological analysis and assessment
689 of the energy impact, *Energy and Buildings* 114 (2016) 191 – 199.
690 doi:doi.org/10.1016/j.enbuild.2015.05.030.
- 691 [40] C. Ferrari, A. Gholizadeh Touchaei, M. Sleiman, A. Libbra, A. Muscio,
692 C. Siligardi, H. Akbari, Effect of aging processes on solar reflectivity
693 of clay roof tiles, *Advances in Building Energy Research* 8 (1) (2014)
694 28–40. doi:10.1080/17512549.2014.890535.
- 695 [41] R. F. De Masi, S. Ruggiero, G. P. Vanoli, Acrylic white paint of in-
696 dustrial sector for cool roofing application: Experimental investigation
697 of summer behavior and aging problem under Mediterranean climate,
698 *Solar Energy* 169 (2018) 468–487. doi:10.1016/j.solener.2018.05.021.
- 699 [42] T. Aoyama, T. Sonoda, Y. Nakanishi, J. Tanabe, H. Take-
700 bayashi, Study on aging of solar reflectance of the self-cleaning
701 high reflectance coating, *Energy and Buildings* 157 (2017) 92–100.
702 doi:10.1016/j.enbuild.2017.02.021.
- 703 [43] X. Yang, C. Vang, D. Tallman, G. Bierwagen, S. Croll, S. Rohlik, Weath-
704 ering degradation of polyurethane coating, *Polymer Degradation and*
705 *Stability* 74 (2001) 341–351. doi:10.1016/S0141-3910(01)00166-5.
- 706 [44] B. Jelle, Accelerated climate ageing of building materials, components
707 and structures in the laboratory, *Journal of Materials Science* 47 (2012)
708 6475–6496. doi:10.1007/s10853-012-6349-7.
- 709 [45] A. L. Pisello, E. Fortunati, C. Fabiani, S. Mattioli, F. Dominici, L. Torre,
710 L. F. Cabeza, F. Cotana, Pcm for improving polyurethane-based cool
711 roof membranes durability, *Solar Energy Materials and Solar Cells* 160
712 (2017) 34 – 42. doi:10.1016/j.solmat.2016.09.036.
- 713 [46] G. Santunione, C. Ferrari, C. Siligardi, A. Muscio, E. Sgarbi, Accel-
714 erated biological ageing of solar reflective and aesthetically relevant
715 building materials, *Advances in Building Energy Research* (2018) 1–
716 18doi:10.1080/17512549.2018.1488616.

- 717 [47] R. Ye, W. Lin, K. Yuan, X. Fang, Z. Zhang, Experimental and numerical
718 investigations on the thermal performance of building plane containing
719 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded graphite composite phase change material, *Ap-*
720 *plied Energy* 193 (2017) 325–335. doi:10.1016/j.apenergy.2017.02.049.
- 721 [48] C. Piselli, V. Castaldo, A. L. Pisello, How to enhance ther-
722 mal energy storage effect of pcm in roofs with varying solar re-
723 flectance: Experimental and numerical assessment of a new roof sys-
724 tem for passive cooling in different climate conditions, *Solar Energy-*
725 *doi:10.1016/j.solener.2018.06.047.*
- 726 [49] R. Ricciu, L. A. Besalduch, A. Galatioto, G. Ciulla, Thermal charac-
727 terization of insulating materials, *Renewable and Sustainable Energy*
728 *Reviews* 82 (2016) 1765–1773. doi:10.1016/j.rser.2017.06.057.
- 729 [50] A. D’Alessandro, A. L. Pisello, C. Fabiani, F. Ubertini, L. F. Cabeza,
730 F. Cotana, Multifunctional smart concretes with novel phase change
731 materials: Mechanical and thermo-energy investigation, *Applied Energy*
732 212 (2018) 1448–1461. doi:10.1016/j.apenergy.2018.01.014.
- 733 [51] M. H. Chung, J. C. Park, Development of PCM cool roof system to con-
734 trol urban heat island considering temperate climatic conditions, *Energy*
735 *and Buildings* 116 (2016) 341–348. doi:10.1016/j.enbuild.2015.12.056.
- 736 [52] A. L. Pisello, V. Castaldo, G. Pignatta, M. Santamouris, F. Cotana, Ex-
737 perimental in-lab and in-field analysis of waterproof membranes for cool
738 roof application and urban heat island mitigation, *Energy and Buildings*
739 114 (2016) 180–190. doi:10.1016/j.enbuild.2015.05.026.
- 740 [53] ASTM D4329-13, Standard practice for fluorescent ultraviolet (uv) lamp
741 apparatus exposure of plastics, Standard, ASTM International, West
742 Conshohocken, PA (2013). doi:10.1520/D4329-13.
- 743 [54] ASTM G154-06, Standard Practice for Operating Fluorescent Light Ap-
744 parathus for UV Exposure of Nonmetallic Materials, Standard, ASTM
745 International, West Conshohocken, PA (2006). doi:10.1520/G0154-12A.
- 746 [55] ASTM E903-12, Standard Test Method for Solar Absorptance, Re-
747 flectance, and Transmittance of Materials Using Integrating Spheres,
748 Standard, ASTM International, West Conshohocken, PA (2012).
749 doi:10.1520/E0903-12.

- 750 [56] Angelantoni Test Technologies, http://www.acstestchambers.com/Product/Prodotto?id_fam=
751 (2012).
- 752 [57] ASTM G173-03(2012), Standard tables for reference solar spectral
753 irradiances: Direct normal and hemispherical on 37° tilted sur-
754 face, Standard, ASTM International, West Conshohocken, PA (2012).
755 doi:10.1520/G0173-03R12.
- 756 [58] A. V. Sá, M. Azenha, H. De Sousa, A. Samagaio, Thermal enhance-
757 ment of plastering mortars with phase change materials: Experimen-
758 tal and numerical approach, *Energy and Buildings* 49 (2012) 1627.
759 doi:10.1016/j.enbuild.2012.02.031.
- 760 [59] ISO 6946:2017, Building components and building elements – Thermal
761 resistance and thermal transmittance – Calculation methods, Standard,
762 International Organization for Standardization, Geneva, CH (2017).
763 URL <https://www.iso.org/standard/40968.html>
- 764 [60] J. F. Kreider, P. S. Curtiss, A. Rabl, Heating and cooling of buildings:
765 design for efficiency, edition, r Edition, Vol. 32, Taylor & Francis Group,
766 2013. doi:10.5860/choice.32-1554.
- 767 [61] V. Castaldo, V. Coccia, F. Cotana, G. Pignatta, A. L. Pisello, F. Rossi,
768 Thermal-energy analysis of natural “cool” stone aggregates as passive
769 cooling and global warming mitigation technique, *Urban Climate* 14.
770 doi:10.1016/j.uclim.2015.05.006.