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# Targeting functionalised carbon nanotubes at the interphase of Textile Reinforced Mortar (TRM) composites

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## Abstract

Performance of textile reinforced inorganic matrix composites depends on the matrix-to-fabric bond strength, the weak chain in the system. In this work, we investigate the role of multi-walled carbon nanotubes (MWCNT) dispersion in an amorphous silica nano-coating for AR-glass and carbon fabric Textile Reinforced Mortar (TRM) composites. Two lime mortars are considered at 56-day curing. Comparative mechanical testing in uni-axial tension show remarkable enhancements in terms of mean ductility, strength and energy dissipation capabilities. Besides, coating successfully prevents telescopic failure and delamination, which significantly narrows data scattering and benefits design limits. Crack pattern analysis reveals that coating promotes diffuse cracking in the specimen, with gradual and progressive damage buildup. Indeed, mean crack width and mean crack spacing are consistently reduced. BET, optical and E-SEM microscopy supports the action mechanism of the coating, that promotes wettability, surface roughening and imparts a remarkable increase in the specific surface area of the reinforcement.

*Keywords:* Textile Reinforced Mortar, Silica nano-coating, Carbon nanotubes, mechanical performance

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## 1. Introduction

Despite the interesting advantages that Textile Reinforced Mortar (TRM) composites display over the well-established class of Fibre Reinforced Polymer (FRP) composite materials [1], their application as externally-bonded reinforcement (EBR) for strengthening and retrofitting of existing structures is rather limited, in light of the poor bonding quality at the fibre-to-matrix interphase [2, 3, 4, 5]. Lack of compatibility between the fibres and the inorganic binder, as well as the presence of coarse aggregates in the mortar, result in unsatisfactory adhesion mechanisms, which trigger inconsistent failure modes, such as fabric delamination and telescopic failure. The latter is the typical failure mechanism in TRM, and consists of inner filaments in the fibres (the core) slipping over outer filaments (the sleeve) that are bonded to the mortar, as in the unfolding of a telescope. Indeed, the spacing between two adjacent fibres within a multifilament yarn (few microns) is several orders of magnitude lower than the average diameter of mortar grains, which is typically around 0.5 – 1 mm. Consequently, mortar is unable to penetrate inside the filaments and bonds rest confined to the sleeve. In addition, poor chemical affinity (i.e. low hydrophilicity of the fibres) prevents from the formation of strong chemical bonds at the interphase, even for sleeve filaments. In contrast to FRP, the poor bonding quality affecting TRM/TRC impairs fibre-matrix congruence during deformation and, as a result, the rule of mixtures cannot be safely adopted to build reliable models [6]. Furthermore, failure occurs unreliably, according to multiple mechanisms, whence elevated scattering ensues. As a result, design limits are strongly penalized and the strengthening potential of the reinforcing fabric remains almost unexploited [7, 8].

A few attempts are documented in the literature to remedy this intrinsic weakness of TRM, most often directed at matrix modification [9, 10], also by CNT addition [11, 12]. In particular, polymeric modification of the inorganic matrix, that is admitted up to 5%wt over the inorganic component by the guidelines [13], goes under the name of Fibre Reinforced Cementitious Matrix

31 (FRCM) [3]. However, fibre coating appears as the most promising approach  
32 to bridge the performance gap between organic and inorganic composites, for  
33 it addresses precisely the matrix-to-fibre interphase. Specifically, capitalizing  
34 over the large body of expertise already developed for FRP, organic coatings  
35 represent the most natural option [14]. Evidence shows that organic coatings  
36 are capable of penetrating in between the reinforcing filaments and effectively  
37 prevent telescopic failure. In Donnini et al. [10], quartz sand is added to epoxy  
38 to roughen the matrix-to-fibre surface. Dvorkin et al. [15] experimentally docu-  
39 ment the reduction of fluid transport of aggressive ions inside carbon filaments  
40 induced by epoxy coating, thus promoting durability. In general, epoxy coatings  
41 have proved remarkably successful in enhancing mechanical performance, also  
42 through healing defects on the fibre surface [16]. Besides, fine-tuning epoxy for-  
43 mulation [17] and viscosity [18] highly improves the overall behaviour of coated  
44 TRM. It is noteworthy that the embedding matrix is capable of shielding the  
45 epoxy coating from the negative effects associated to high temperature exposure  
46 [19].

47 Nonetheless, the presence of an organic component is generally undesirable,  
48 mostly on the same grounds by which organic matrices are being replaced by  
49 inorganic binders. As a result, much interest lies in investigating inorganic  
50 coatings. As an example, silicon dioxide (in the form of micro-silica fume and  
51 silica nano-particles) exploits concentrated pozzolanic reactivity to good advan-  
52 tage, by strengthening the interphase zone (IZ), namely the thin mortar layer  
53 surrounding each fibre [20, 21]. Owing to its pronounced hydrophilic nature,  
54 silica appears as a promising fully-inorganic coupling agent, especially for alkali  
55 resistant glass (ARG) fabrics [22]. The addition of nano-fillers in the coating  
56 formulation can also be pursued and preliminary investigations are ongoing. In  
57 the paper by Cohen and Peled [23], mechanical performance of textile reinforced  
58 concrete (TRC) is assessed against the application of organic and inorganic  
59 nanofillers for inducing high friction resistance. Nano-particles suitable for this  
60 purpose comprise, among many, carbon-based fillers or organoclays [24, 25, 26].  
61 In particular, multi-walled carbon nanotubes (MWCNT) are nested concen-

62 tric single-wall graphene hollowed particles with high aspect ratio (around 500)  
63 and specific surface area [27, 28]. Their outstanding tensile strength and stiff-  
64 ness, combined with negligible mass, make for a promising reinforcing technique  
65 [29, 30].

66 Kostopoulos et al. [31] highlight the role of MWCNT at improving impact  
67 and post-impact resistance of carbon FRP for aerospace applications. As dis-  
68 cussed in the exhaustive review by Liew et al. [32], the adoption of CNTs in  
69 cementitious materials has been investigated only in fairly recent times, as an  
70 attempt at reducing micro-cracking within the conglomerate. In addition, CNT  
71 successfully dispersed in concrete have proved to improve the damping proper-  
72 ties of cementitious composites [33]. This outcome is mainly due to the bridging  
73 effect exerted by CNT at the nanoscale and to the simultaneous reduction of  
74 the core porosity of the conglomerate [34, 35]. In a recent paper, Cui et al. [36]  
75 thoroughly examine how geometrical properties (e.g. tubes length and diam-  
76 eter) as well as functionalisation techniques of MWCNT tune the compressive  
77 and flexural response of concrete. According to these findings, the optimum as-  
78 pect ratio of nanotubes should range at about 100 and hydroxyl-functionalised  
79 (namely highly hydrophilic) nanotubes convey remarkable strength gains, since  
80 the hydration products are diffusely and firmly bonded to the nano-fillers sur-  
81 face. Han et al. [37] point out that a CNT interpenetrated network in the  
82 conglomerate core favours leakage of hydration heat, thus reducing autogenous  
83 cracking. Finally, electrical conductivity of CNTs may impart smart sensing  
84 capabilities to structures, which become able to detect damage and incipient  
85 failure by carrying out time-scheduled non-destructive resistance measurements  
86 (see e.g. [38, 39] and references therein). Within the framework of cementitious  
87 materials, Irshidat and Al-Shannaq [40] study the dispersion of CNTs in the  
88 cementitious embedding mortar of textile composites and provide strong evi-  
89 dence as to performance and durability enhancements. In the subsequent paper  
90 [12], they present the findings of an experimental program concerning bend-  
91 ing of reinforced concrete (RC) beams strengthened with MWCNT-modified  
92 TRM laminates. As far as 1-ply laminates are concerned, the most impressive

93 results regards the initial stiffness of the reinforced beam, rather than the flex-  
94 ural capacity, which appears highly sensitive to the binder’s formulation. All  
95 the aforementioned contributors agree on the fundamental role played by surfac-  
96 tants, which unlock the remarkable benefits of well dispersed unbundled CNTs  
97 [41, 42, 43].

98 In this paper, we consider a 0.5% wt. stabilized suspension of MWCNTs  
99 in an amorphous silica coating solution for application on synthetic continuous  
100 fibres, namely alkali resistant (AR) glass and carbon. In contrast to the existing  
101 literature, we consider a functionalised dispersing medium (i.e. silica sol) and  
102 modification is restricted to the fibres’ surface, as opposed to modification of the  
103 embedding matrix. Compared to control specimens, remarkable improvements  
104 in terms of ultimate strength, ductility and energy dissipation capability are  
105 found. This outcome is related to a dramatic increase of the fabric specific  
106 area, accompanied by important enhancement in terms of hydrophilicity, i.e.  
107 the capacity to establish stronger chemical fibre-to-matrix cross-links. Optical  
108 and E-SEM microscopy reveal that CNT-induced surface roughness effectively  
109 prevents telescopic failure and fabric slippage inside the matrix.

## 110 **2. Materials and methods**

### 111 *2.1. Materials*

112 Two different fine-grained lime-based mortars and two reinforcing textiles  
113 are considered.

114 Physical, compositional and mechanical properties are gathered in Table 1.  
115 The first mortar, labelled MS (Lime Mortar,  $f_{ck} = 5$  MPa), consists of a natural  
116 hydraulic lime-based mortar with siliceous and carbonatic aggregates. Cement  
117 content is lower than 5%wt. The second mortar, tagged GC (Hybrid Mortar,  
118  $f_{ck} = 15$  MPa), presents coarse aggregates (up to 1.4 mm diameter) and blended  
119 lime and cement binder [17].

120 Two different multifilament fabrics are considered as the reinforcing phase  
121 (Figure 1): AR glass (G) balanced biaxial mesh with open square grid and high-  
122 tenacity carbon (C) uniaxial fabric with ARG yarns in the weft direction. The

| Characteristic                               | Unit               | MS   | GC   |
|--|--------------------|------|------|
| Aggregate maximum size                       | mm                 | 1.0  | 1.4  |
| Density (fresh state, UNI 1015-6)            | kg/dm <sup>3</sup> | 1.50 | 1.73 |
| Min. compression strength at 28 days         | MPa                | 5.0  | 15.0 |
| Min. flexural strength at 28 days (EN 196/1) | MPa                | 1.0  | 3.4  |
| Adhesion strength at 28 days                 | MPa                | 0.4  | 1.0  |
| Water content                                | %                  | 21   | 21   |
| Longitudinal elastic modulus (EN 13412)      | GPa                | n.a. | 9.0  |

Table 1: Mortars' properties (as provided by the manufacturer)

123 main mechanical properties of the fabrics are displayed in Table 2. Fabrics are  
124 coated with a sol-gel silica solution where MWCNTs are dispersed. MWCNTs  
125 (Sigma, Merck Group) properties are reported in Table 3.

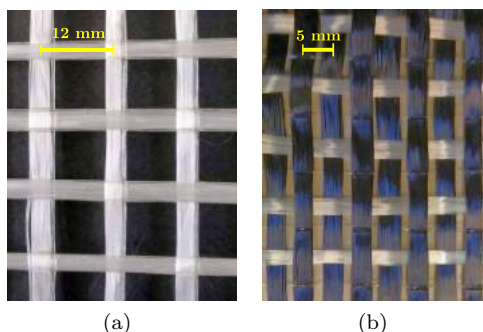


Figure 1: AR-glass (a) and carbon (b) multifilament fabrics are considered as the reinforcing phase

126 *2.2. Amorphous silica nano-coating with dispersed MWCNT*

127 CNT dispersion is obtained taking advantage of the water excess required  
128 to accommodate hydrolysis of the acid-catalysed silica sol-gel. A stable CNT  
129 aqueous dispersion is obtained by adding sodium dodecyl benzene sulfonate  
130 (NaDBS) as surfactant, as reported in the research by Haghgoo et al. [44]. In a  
131 covered beaker, a 3.3%wt solution (with respect to deionized water) of CNTs is  
132 mixed with NaDBS powder in a 2:3 CNT/NaDBS weight ratio. The suspension  
133 is placed on a magnetic stirrer for 5 minutes and then sonicated for 60 minutes,  
134 in order to allow the surfactant to distribute within the nanotubes interstices  
135 and favour disaggregation [45]. The suspension is added to TEOS/isopropyl

| Characteristic   | Unit                | G     | C     |
|--|---------------------|-------|-------|
| Yarn count   | g/km                | 1200  | 800   |
| Total (warp) specific weight per unit fabric area        | g/m <sup>2</sup>    | 300   | 220   |
|  |                     | (150) | (150) |
| Grid spacing (along the warp direction)                  | mm                  | 12    | 5     |
| Dry fabric cross-sectional area (per unit width), $A_f$  | mm <sup>2</sup> /cm | 0.72  | 0.88  |
| Ultimate strength along warp with epoxy (per unit width) | kN/cm               | 0.72  | 1.80  |
| Elastic modulus, $E_f$                                   | GPa                 | 74    | 240   |

Table 2: Multifilament fabrics properties (as provided by the manufacturer)

| Characteristic      | Unit              | Value       |
|---------------------|-------------------|-------------|
| Density (at 25°C)   | g/cm <sup>3</sup> | 2.1         |
| Bulk density        | g/cm <sup>3</sup> | 0.06 ÷ 0.08 |
| Outside diameter    | nm                | 10          |
| Inside diameter     | nm                | 4           |
| Length              | nm                | 4000        |
| Aspect ratio        | –                 | 350 ÷ 550   |
| Walls               | No.               | 6 ÷ 8       |
| Surface area (BET)  | m <sup>2</sup> /g | 280 ÷ 350   |
| Surface resistivity | Ω/sq              | 700 ÷ 900   |
| Melting Point       | °C                | 3652 ÷ 3697 |

Table 3: Multi-walled carbon nanotubes properties (as provided by the manufacturer)

136 alcohol solution together with nitric acid in stoichiometric ratio to trigger sol-  
137 gel transition, see also [46]. The silica solution, with an overall CNT weight  
138 ratio of 0.5%, is stirred for 2 hours at 50°C and then sonicated for further 15  
139 minutes before fibres’ dip-coating. Cut-to-size textiles are then immersed for 5  
140 minutes in the suspension and subsequently left at laboratory conditions for a  
141 few minutes. Finally, fabrics are dried in a muffle at 110 °C for 15 minutes.

### 142 2.3. Experimental programme

#### 143 2.3.1. Coating quality assessment

144 Fibre hydrophilicity is measured through a Brunauer-Emmett-Teller (BET)  
145 analysis [47], which is commonly used to gain insight on the specific (per unit  
146 mass) surface area (SSA) of a solid. SSA is an indicator of the adsorption and  
147 of the reactive capability of a surface. BET provides an accurate evaluation of



148 the SSA of a material at the solid phase by expressing its nitrogen adsorption  
149 as a function of relative pressure. SSA is evaluated by computing the amount  
150 of adsorbate gas corresponding to a monomolecular layer on the surface of the  
151 material. This technique encompasses both external surface and pore area to  
152 determine the total SSA. Fabric specimens weighting between 0.5 and 1 g are  
153 coated and then dried overnight at 60°C to remove residual humidity. Finally,  
154 measurement is performed in a Gemini V2.00 porosimeter (Micromeritics) on  
155 both uncoated and MWCNT coated fabric. Coating quality and uniformity are  
156 determined through optical stereo-microscopy (Leica EZ4D) and environmental  
157 scanning electron microscopy (E-SEM, Quanta-200, Fei Company).

### 158 *2.3.2. Mechanical testing*

159 Comparative uni-axial tensile tests are carried out on TRM specimens with  
160 (S-CNT) and without (control group, UC) silica coating with dispersed MWC-  
161 NTs. Specimens are manufactured on an individual basis by means of a dis-  
162 mountable polyethylene formwork and each test group consists of at least four  
163 specimens. 1-ply prismatic laminates are manufactured following the recent  
164 guidelines [48, 49], as detailed in [50, 51]:

- 165 • The first layer of fresh mortar is applied on the lubricated formwork in  
166 between two constraining removable laths, which provide guideline for the  
167 prescribed thickness of the embedding layer and for fabric placing.
- 168 • The reinforcing textile, either uncoated (UC) or S-CNT pre-preg, is placed  
169 on the fresh mortar onto which it is gently pressed to promote mortar  
170 interlocking.
- 171 • The mortar over-layer is then applied in between a second set of constrain-  
172 ing laths, that is stacked on top of the first.
- 173 • Specimens are cured for 7 days, tightly wrapped in a polypropylene self-  
174 detaching bag to simulate moist-curing.
- 175 • Finally, specimens are stripped and stored at laboratory conditions ( $T =$

176  $(20 \pm 2)^\circ\text{C}$ ,  $RH = (65 \pm 5)\%$ ) for 49 days. Indeed, 56-day curing is proven  
177 to positively affect durability for lime-based composite laminates [52].

- 178 • Prior to testing, two pairs of 100-mm long G-FRP tabs are epoxy glued  
179 at the specimen ends to accommodate the gripping mechanism at testing.

180 Specimens have prismatic shape (coupons), are 7-mm thick and their gauge  
181 length is  $L_g = 250$  mm. Width equals 36 mm or 32 mm, and it is designed as to  
182 accommodate 3 or 7 strands, respectively for ARG and carbon fabric. Tensile  
183 tests are carried out on an electro-mechanic Instron 5567 universal testing ma-  
184 chine (UTM), equipped with a 30 kN load cell. The clamping system consists  
185 of two hinges connected with stainless steel wedge clamps that apply lateral  
186 friction to the laminates. The test set-up is compliant with the prescriptions  
187 of the most common guidelines for characterization of Fibre Reinforced Cemen-  
188 titious Matrix (FRCM) composite materials [53]. Tests are carried out under  
189 displacement control at the nominal displacement rate of 0.50 mm/min. DIC  
190 analysis lends the actual elongation rate by subtracting the contribution of the  
191 sliding motion at the clamp-to-coupon interface. The latter is usually about  
192 10% of the nominal rate [54].

193 Before embedment, uncoated and pre-preg (coated) fabrics are investigated  
194 through optical stereo-microscope LEICA EZ4D and environmental scanning  
195 electron microscope (E-SEM, Quanta FEI, The Netherlands) to evaluate the  
196 quality of the surface coating. During testing, the crack pattern evolution is  
197 recorded by DIC. Finally, failed specimens are investigated through optical mi-  
198 croscopy, in order to characterise the distribution of carbon nanoparticles on  
199 the fibres surface and the quality of the impregnation.

### 200 **3. Results and discussion**

#### 201 *3.1. Coating characterization*

##### 202 *3.1.1. Surface analysis and hydrophilicity*

203 The effect of the coating on the SSA is well illustrated in the bar-charts  
204 presented in Fig.2, where a logarithmic scale is adopted. A remarkable increase

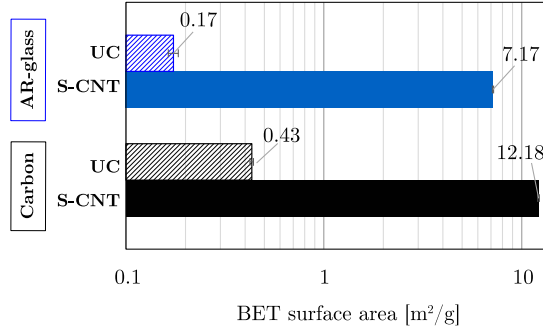


Figure 2: Specific surface area (SSA) for uncoated (UC) and silica+carbon nanotubes (S-CNT) coated fabrics, as obtained by BET analysis (logarithmic scale)

205 of the surface area is clearly achieved through S-CNT coating, and the relative  
 206 outcome is even more pronounced for glass fibres. This outcome is not entirely  
 207 unexpected given the affinity of glass with silica. Coating conveys a surface  
 208 area enhancement that fares about 40 and 27 times the SSA of the control  
 209 group, respectively for glass and carbon. This notable increase of surface area  
 210 may effectively promote the hydrophilicity of the fabric and thus the adhesion  
 211 capacity at the interphase. The accuracy of BET measurements is supported  
 212 by the coefficient of determination in the linear regression of the BET diagram  
 213 ( $v^{-1}\varphi(1-\varphi)^{-1}$  vs  $\varphi$ ), that is practically 1 except for the G-UC sample ( $R^2 =$   
 214 0.794), due to the extremely low SSA. In the BET diagram,  $v$  represents the mass  
 215 of adsorbed gas and  $\varphi$  is the ratio between the equilibrium and the saturation  
 216 pressure of adsorbates at the temperature of adsorption [47]. Typical BET  
 diagrams are presented in Figure 3.

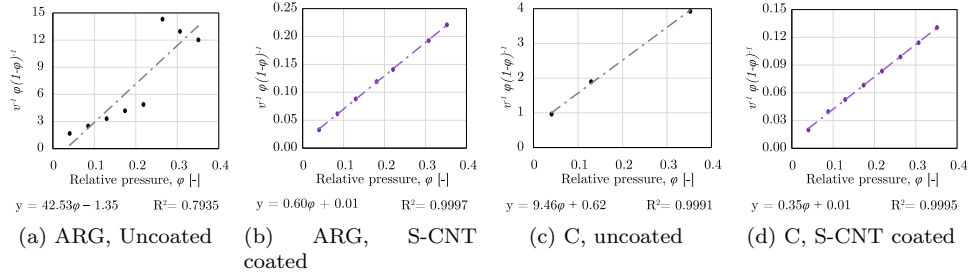


Figure 3: BET diagrams for all the tested groups

218 *3.1.2. Optical and E-SEM microscopy*

219 Quality and uniformity of the coating are investigated through optical and  
220 electron microscopy. Figures 4(a) and (c) present an optical investigation of  
221 the surface of uncoated glass and uncoated carbon textiles, respectively, to be  
222 compared with the corresponding coated specimens, Fig.4(b) and (d). In the  
223 case of glass fibres, the presence of bundles of CNT, which stand out of the clear  
224 background, is quite evident. Conversely, CNT presence on carbon fibres can  
225 be appreciated only when light shines at a large incident angle to the sample  
226 surface. Sharper results are obtained through E-SEM: Figure 5 shows a sin-  
227 gle carbon coated multifilament yarn at 1000 $\times$  and 4000 $\times$  magnification. The  
228 presence of CNT individual nano-particles cannot be singled out, most likely  
229 as a result of the embedding role of silica molecules that surround CNTs. Yet,  
230 fibres appear coated by a thin layer of silica, which can penetrate inside the  
231 inner part of the yarn. Patches of residual salt deposits, most likely due to  
232 the surfactant employed to disperse CNTs, are seldom identified on the fibres  
233 through an energy dispersive X-ray (EDX) microanalysis.

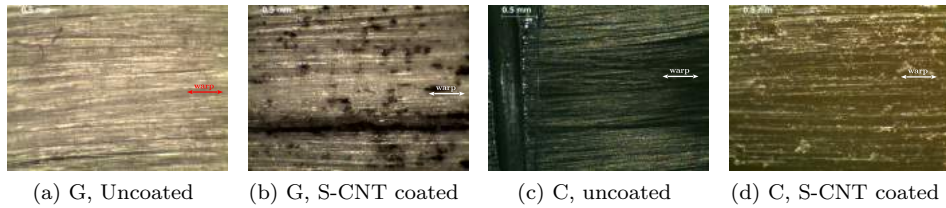


Figure 4: Optical stereo-microscopy investigation for AR-glass (a-b) and carbon (c-d) fabrics without and with S-CNT coating

234 *3.2. Mechanical tests*

235 *3.2.1. Glass fabric*

236 Figure 6 presents mean strength (i.e. stress-strain) curves for AR-glass tex-  
237 tiles embedded in MS and GC mortar. An almost perfectly tri-stage behaviour  
238 is consistently observed across the S-CNT coated groups. The first stage is elas-  
239 tic and it holds until the first cracking strength (FCS) is attained. The elastic  
240 stage is followed by an intermediate regime (cracking stage) characterized by

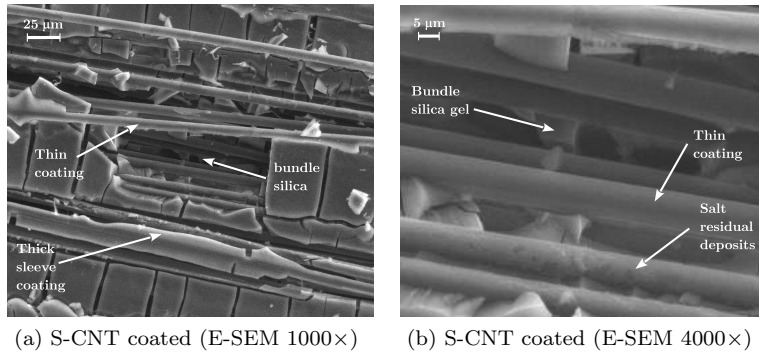


Figure 5: E-SEM investigation for carbon fabrics with S-CNT coating

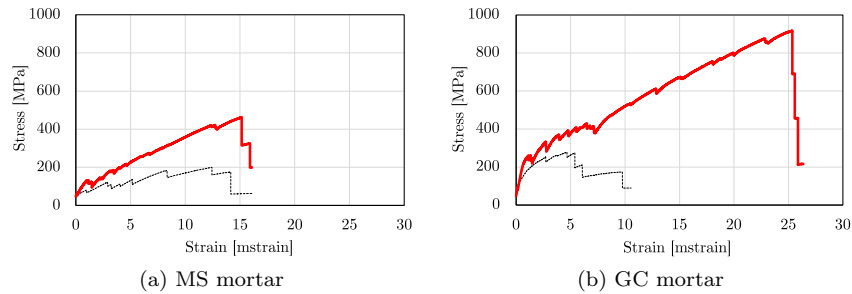


Figure 6: Mean stress-strain curves for uncoated (UC, black fine-dashed) and coated (S-CNT, red solid) glass fabric-reinforced coupons. (1 mstrain =  $10^{-3}$  mm/mm)

241 the opening of several successive cracks. This regime ends when new cracks  
 242 cease to appear and the existing ones widen. In this final, post-cracking stage,  
 243 the specimen is more compliant (i.e. less stiff) than in the elastic regime, owing  
 244 to the absence of the mortar contribution. The formation of several new cracks  
 245 at the cracking stage is supported by many small stress drops in the strength  
 246 curve, which account for the appearance of a diffuse cracking pattern. This,  
 247 in turn, leads to high levels of mechanical energy being dissipated at failure  
 248 (toughness) [55]. In stark contrast, the cracking stage appears very shortly in  
 249 the uncoated specimens, where wide-spaced large cracks immediately develop  
 250 with irreversible damage to the interphase, as a consequence of the high bursts  
 251 of mechanical energy that are being released and cannot be dealt with elastically  
 252 by the interphase. Accordingly, failure at the interphase brings about detach-  
 253 ment between the fabric and the embedding mortar, sliding of the fibres and

254 internal delamination. On the overall, this mechanism possesses a lower bearing  
 255 capacity than that in the coated group. For these reasons, CNT-coating pro-  
 256 vides remarkable improvement both in terms of strength and ductility, that is  
 particularly striking for the hybrid lime-cement mortar (namely, mortar G).

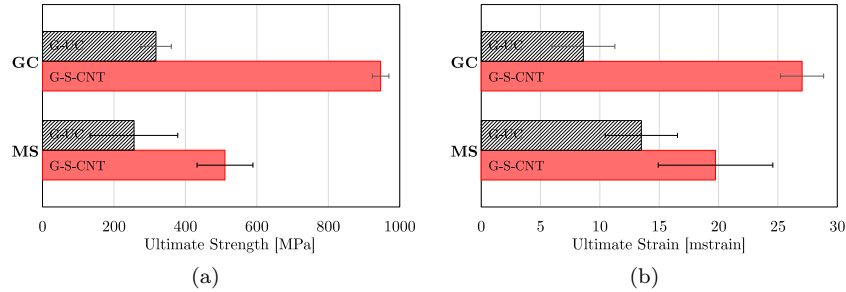


Figure 7: Ultimate strength (a) and strain (b) with  $\pm 1$  standard deviation band for uncoated (UC, grey) and coated (S-CNT, red) groups for all G-TRM.

257

258 A bar-chart comparison of the mean ultimate tensile strength (UTS) and  
 259 elongation of G-TRM composites at failure is presented in Figure 7. Labels  
 260 code for mortar (GC or MS), reinforcing fabric (G or C) and coating (S-CNT)  
 261 or lack thereof (UC). For example, GC-G-UC stands for GC-matrix reinforced  
 262 with uncoated glass fabric. It is very important to observe that coating sig-  
 263 nificantly decreases data scattering, especially for GC mortar, and this has a  
 264 strong positive bearing on design limits [21]. In fact, this very outcome is es-  
 265 pecially valuable for TRC/TRM materials, whose inconsistent performance is  
 266 their major drawback.

267 The beneficial effect of the coating on mechanical performance of G-TRM  
 268 specimens is best appreciated through the data provided in Table 4, which  
 269 compares the mean ultimate tensile strength,  $\mu(f_u)$ , mean elongation,  $\mu(\varepsilon_u)$ ,  
 270 and mean dissipated energy,  $\mu(W_u)$ , across all tested groups, together with the  
 271 relevant standard deviation. There,  $\mu(\cdot)$ ,  $\varsigma(\cdot)$  and CoV represent the mean  
 272 value, the standard deviation and the coefficient of variation of the sampling,  
 273 respectively;  $\Delta(\cdot)$  provides the percent variance of the relevant quantity in the  
 274 coated against the uncoated group. In order to take into account data scattering,  
 275 characteristic values (5%-fractile) are computed through Eqn.(1), assuming that

| <b>m</b>  | <b>UC</b>                          |  |            |                                   | <b>S-CNT</b>                       |  |            |                                   | <b><math>\Delta</math></b>        |                                  |
|-----------|------------------------------------|--|------------|-----------------------------------|------------------------------------|--|------------|-----------------------------------|-----------------------------------|----------------------------------|
|           | $\mu(f_u)$<br>[MPa]                | $\varsigma(f_u)$<br>[MPa]                | CoV<br>[%] | $f_{u,k}$<br>[MPa]                | $\mu(f_u)$<br>[MPa]                | $\varsigma(f_u)$<br>[MPa]                | CoV<br>[%] | $f_{u,k}$<br>[MPa]                | $\Delta\mu(f_u)$<br>[%]           | $\Delta f_{u,k}$<br>[%]          |
| <b>MS</b> | 256                                | 123                                      | 48         | 54                                | 511                                | 78                                       | 15         | 383                               | +100                              | +600                             |
| <b>GC</b> | 317                                | 43                                       | 14         | 246                               | 947                                | 23                                       | 2          | 909                               | +198                              | +270                             |
|           | $\mu(\varepsilon_u)$<br>[mstrain]  | $\varsigma(\varepsilon_u)$<br>[mstrain]  | CoV<br>[%] | $\varepsilon_{u,k}$<br>[mstrain]  | $\mu(\varepsilon_u)$<br>[mstrain]  | $\varsigma(\varepsilon_u)$<br>[mstrain]  | CoV<br>[%] | $\varepsilon_{u,k}$<br>[mstrain]  | $\Delta\mu(\varepsilon_u)$<br>[%] | $\Delta\varepsilon_{u,k}$<br>[%] |
| <b>MS</b> | 13.5                               | 3.0                                      | 23         | 8.6                               | 19.7                               | 4.8                                      | 24         | 11.8                              | +46                               | +38                              |
| <b>GC</b> | 8.6                                | 2.7                                      | 31         | 4.2                               | 27.0                               | 1.8                                      | 7          | 24.0                              | +214                              | +476                             |
|           | $\mu(W_u)$<br>[J/mm <sup>3</sup> ] | $\varsigma(W_u)$<br>[J/mm <sup>3</sup> ] | CoV<br>[%] | $W_{u,k}$<br>[J/mm <sup>3</sup> ] | $\mu(W_u)$<br>[J/mm <sup>3</sup> ] | $\varsigma(W_u)$<br>[J/mm <sup>3</sup> ] | CoV<br>[%] | $W_{u,k}$<br>[J/mm <sup>3</sup> ] | $\Delta\mu(W_m)$<br>[%]           | $\Delta W_{u,k}$<br>[%]          |
| <b>MS</b> | 2.10                               | 1.11                                     | 53         | 0.28                              | 5.93                               | 1.15                                     | 19         | 4.0                               | +183                              | +1346                            |
| <b>GC</b> | 2.65                               | 0.60                                     | 22         | 1.67                              | 16.1                               | 0.91                                     | 6          | 14.6                              | +508                              | +777                             |

Table 4: Glass reinforcement – Mean UTS  $\mu(f_u)$ , mean strain  $\mu(\varepsilon_u)$  and mean dissipated energy  $\mu(W_u)$  across all tested groups, alongside their standard deviation  $\varsigma$ , coefficient of variation CoV and percent variance  $\Delta$ .  $f_{u,k}$  is the characteristic strength in a normal distribution

276 data are normally distributed [56].

$$(\cdot)_k = \mu(\cdot) - 1.64 \varsigma(\cdot) \quad (1)$$

277 The corresponding percent variance of the coated vs the uncoated group is  
278 denoted by  $\Delta f_{u,k}$ . We observe a striking five-fold increase in the mean dissi-  
279 pated energy for coated specimens embedded in the GC mortar against uncoated  
280 ones, as a combination of enhanced ultimate strength (+198%) and elongation  
281 (+214%). For the MS mortar, the corresponding result is also very significant,  
282 albeit not so impressive (+183%). Most significantly, data scattering is also  
283 strongly reduced by CNT-coating: consideration of the CoV for strength in  
284 the MS mortar (GC mortar) jumps from 48% (14%) in the UC group to 15%  
285 (2%) in the coated group. Similar observations can be made for elongation and  
286 energy dissipation. Such results support the idea that consistency in ultimate  
287 performance is strictly connected to the suppression of telescopic failure and of  
288 intralaminar textile sliding, which are inherently inconsistent mechanisms.

289 Stereo-microscopy provides clear evidence of interphase compatibility im-  
290 provement, as in Figs.8 and 9 referring to the surface of glass fibres emerging in

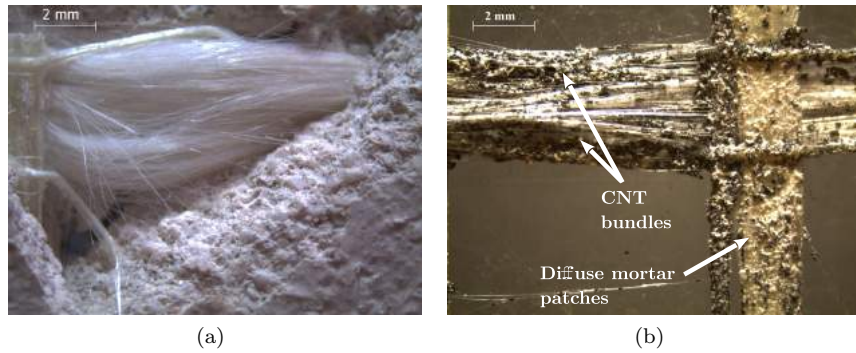


Figure 8: 8X magnification of uncoated (a) and coated (b) glass yarns at failure.

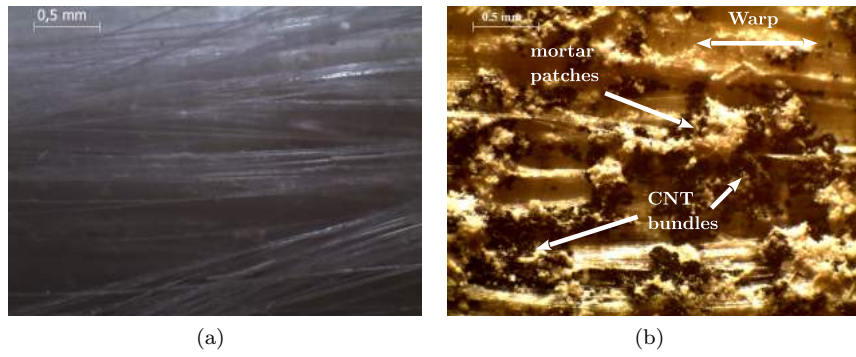


Figure 9: 35X magnification of uncoated (a) and coated (b) glass yarns at failure.



291 the failure zone. Indeed, while UC strands are clean as they have been “pulled-  
 292 out” as a result of telescopic sliding (unfolding generates misalignment of the  
 293 filaments of a single yarn), fibres in the S-CNT group maintain good alignment  
 294 and to them many mortar patches and CNT bundles are diffusely attached.  
 295 The distribution of MWCNTs appears not uniform over the fibre surface, which  
 296 fact enhances micro-roughness and prevents slippage with the mortar at the  
 297 interphase. In addition to providing a functionalising dispersing medium, silica  
 298 enhances the chemical interlocking with the mortar and bonds fibres together  
 299 [46]. To these benefits, the contribution of CNT is superposed and it consists of  
 300 strengthening the interphase zone and the fibre-to-matrix adhesion capability.

301 *3.2.2. Carbon fibres*

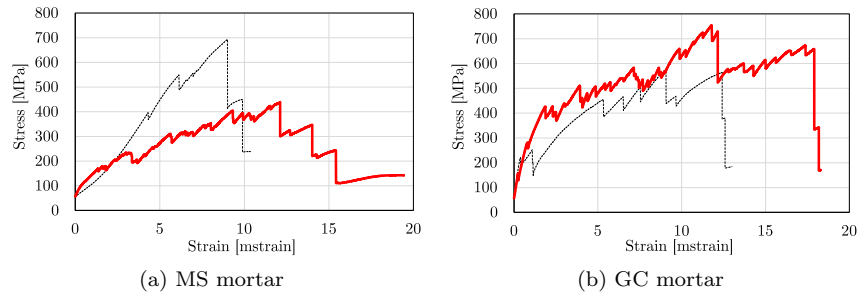


Figure 10: Mean stress-strain curves for uncoated (UC, black fine-dashed) and coated (S-CNT, red solid) carbon-fabric reinforced specimens

302 Similar considerations may be put forward with regard to specimens rein-  
 303 forced with uniaxial carbon fabric. However, as already observed in Signorini  
 304 et al. [51], silica coating appears less effective on carbon fabric than on AR-  
 305 glass. This can be ascribed to the lower chemical affinity of the silica-carbon  
 306 system, as compared to silica-glass. In fact, the latter is expected to perform  
 307 significantly better, as a result of the chemical composition of the coating and  
 308 of the substrate being essentially the same. A consistent picture emerges when  
 309 MWCNTs act as high-strength interphase nanofillers in the coating. Figure  
 310 10 presents the mean stress-strain curve in uni-axial tension obtained for ms  
 311 and GC mortars. Strikingly, coating impairs performance in the MS mortar,  
 312 although this negative outcome is compensated by significant benefits in terms

313 of ductility and the overall effect is positive for mean energy dissipation (yet  
 314 neutral in terms of characteristic value) .

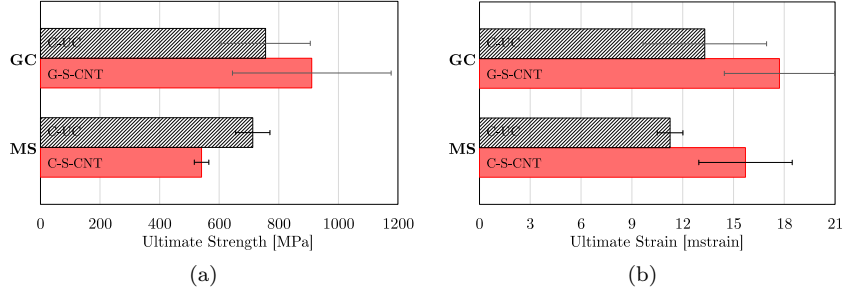


Figure 11: Mean ultimate strength (a) and strain (b) with  $\pm 1$  standard deviation bands for uncoated (UC, grey) and coated (S-CNT, red) carbon fabric reinforced specimens

315 For better comparison, bar-charts are given in Figure 11 which illustrate  
 316 ultimate performance alongside standard deviation bands for the MS and GC  
 317 mortars. Data on mean ultimate strength, elongation and specific energy dissi-  
 318 pated at failure are gathered in Table 5, where the percentage variance is also  
 319 given. Again, characteristic values are computed following Eqn.(1).

320 In general, a positive effect is still brought by CNT-coating on carbon fabric  
 321 specimens. However, data scattering shows a mixed response. Interestingly,  
 322 S-CNT coating is most advantageous for mortar G, which is characterized by  
 323 higher nominal compressive strength and stiffness and lower nominal ductility.  
 324 This seems to partly contrast the observations drawn by Signorini et al. [46],  
 325 according to which best performance is associated to higher lime content in the  
 326 binder. However, in contrast to the present study, Signorini et al. [46] employ a  
 327 high compressive strength mortar which contains glass microfibers. Indeed, the  
 328 benefit of adding dispersed microfibres to the mortar in terms of tensile response  
 329 is well-documented in the literature [57, 58]. It is therefore concluded that me-  
 330chanical performance in traction of the embedding mortar plays a fundamental  
 331 role in determining the overall tensile response of the composite.

332 In the case of both mortars, coating brings about a significant increase in the  
 333 mean ultimate elongation, that is +40% for MS and +33% for GC. In terms of  
 334 ultimate strength, coating induces an unexpected 24% UTS loss for mortar MS.

| <b>m</b>  | <b>UC</b>                          |  |            |                                   | <b>S-CNT</b>                       |  |            |                                   | <b><math>\Delta</math></b>    |                                   |
|-----------|------------------------------------|--|------------|-----------------------------------|------------------------------------|--|------------|-----------------------------------|-------------------------------|-----------------------------------|
|           | $\mu(f_u)$<br>[MPa]                | $\varsigma(f_u)$<br>[MPa]                | CoV<br>[%] | $f_{u,k}$<br>[MPa]                | $\mu(f_u)$<br>[MPa]                | $\varsigma(f_u)$<br>[MPa]                | CoV<br>[%] | $f_{u,k}$<br>[MPa]                | $\Delta f_m$<br>[%]           | $\Delta f_{u,k}$<br>[%]           |
| <b>MS</b> | 713                                | 58                                       | 8          | 618                               | 540                                | 24                                       | 5          | 501                               | -24                           | -19                               |
| <b>GC</b> | 756                                | 150                                      | 20         | 510                               | 911                                | 266                                      | 29         | 475                               | +20                           | -7                                |
|           | $\mu(\varepsilon_u)$<br>[mstrain]  | $\varsigma(\varepsilon_u)$<br>[mstrain]  | CoV<br>[%] | $\varepsilon_{u,k}$<br>[mstrain]  | $\mu(\varepsilon_u)$<br>[mstrain]  | $\varsigma(\varepsilon_u)$<br>[mstrain]  | CoV<br>[%] | $\varepsilon_{u,k}$<br>[mstrain]  | $\Delta \varepsilon_m$<br>[%] | $\Delta \varepsilon_{u,k}$<br>[%] |
| <b>MS</b> | 11.3                               | 0.8                                      | 7          | 10                                | 15.7                               | 2.8                                      | 18         | 11.1                              | +40                           | +11                               |
| <b>GC</b> | 13.3                               | 3.7                                      | 27         | 7.2                               | 17.7                               | 3.3                                      | 18         | 12.3                              | +33                           | +70                               |
|           | $\mu(W_u)$<br>[J/mm <sup>3</sup> ] | $\varsigma(W_u)$<br>[J/mm <sup>3</sup> ] | CoV<br>[%] | $W_{u,k}$<br>[J/mm <sup>3</sup> ] | $\mu(W_u)$<br>[J/mm <sup>3</sup> ] | $\varsigma(W_u)$<br>[J/mm <sup>3</sup> ] | CoV<br>[%] | $W_{u,k}$<br>[J/mm <sup>3</sup> ] | $\Delta W_m$<br>[%]           | $\Delta W_{u,k}$<br>[%]           |
| <b>MS</b> | 3.94                               | 0.40                                     | 10         | 3.28                              | 4.91                               | 1.05                                     | 21         | 3.19                              | +25                           | -3                                |
| <b>GC</b> | 8.74                               | 3.06                                     | 35         | 3.72                              | 23.54                              | 11.64                                    | 49         | 4.45                              | +169                          | +20                               |

Table 5: Carbon reinforcement – Mean ultimate tensile strength  $\mu(f_u)$ , mean strain  $\mu(\varepsilon_u)$  and mean dissipated energy  $\mu(W_u)$  across all tested groups, alongside their standard deviation  $\varsigma$ , coefficient of variation CoV and percent variance  $\Delta$ .  $f_{u,k}$  is the characteristic strength in a normal distribution

335 However, this detrimental bearing is outweighed by ductility enhancement so  
336 that the combined effect works out beneficial on toughness (i.e. energy dissipa-  
337 tion), that is still improved of about 25%. The outcome is far more impressive  
338 for GC mortar, for which toughness increases by 169%, ductility by 70% and  
339 UTS by a mere +20%.

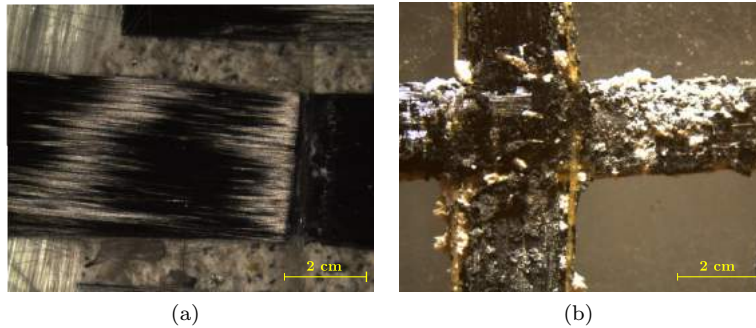


Figure 12: 8X magnification of uncoated (a) and coated (b) carbon yarns at failure.

340 Optical microscopy depicts a scenario that is consistent with the findings  
341 provided by mechanical tests. Fig.12 and 13 show fibres emerging from failed  
342 C-TRM specimens with GC mortar at 8X and 35X magnification, respectively.

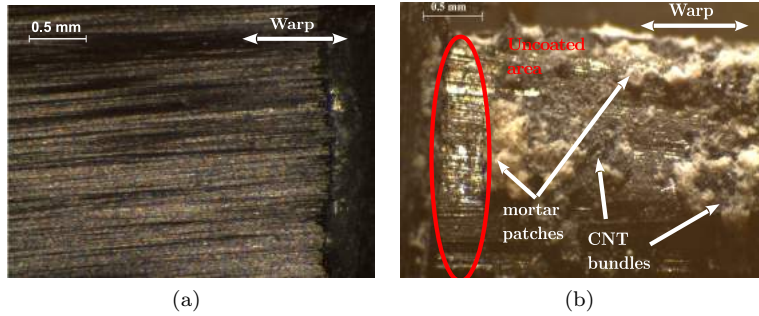


Figure 13: 35X magnification of uncoated (a) and coated (b) carbon yarns at failure.

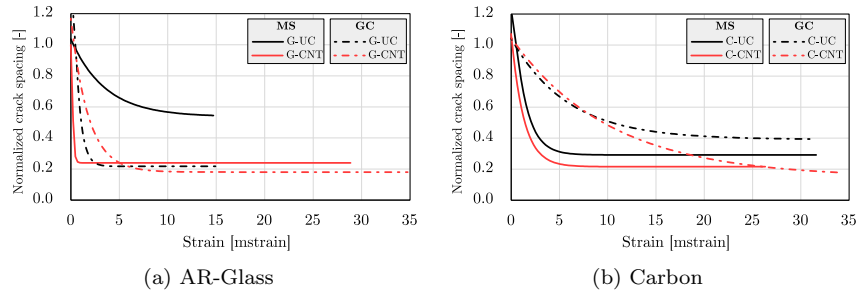


Figure 14: Mean crack spacing (data fit) as a function of strain during testing of AR-glass (a) and carbon (b) specimens in GC mortar. Uncoated specimens are represented with black lines, whilst S-CNT ones with red lines. For the sake of comparison, relevant groups have the same line type (e.g. solid for GC mortar and dash-dotted for MS mortar).

343 Despite generally good impregnation of the coated yarns, supported by the  
 344 presence of diffuse mortar patches on the surface, wide zones still exist where  
 345 the coating is not attached any mortar grain (see detail in Figure 13(b)). These  
 346 areas suggest random lack of adhesion, possibly accompanied by the occurrence  
 347 of slippage, and either phenomenon is attached to large data scattering. Also,  
 348 the strength curve exhibits a blurred behaviour where the three stages are no  
 349 longer well distinct.

### 350 3.3. Crack analysis

351 The evolution of the crack pattern during tensile testing provides information  
 352 about incipient damage mechanisms correlated with matrix-to-fabric adhesion.  
 353 Two important features are identified by DIC post-processing: the average crack  
 354 spacing, which is related with the interphase bond and the apparent composite

| Mortar/Fabric | UC            |                 |              | S-CNT         |                 |              |
|---------------|---------------|-----------------|--------------|---------------|-----------------|--------------|
|               | $S_1$<br>[mm] | $\alpha$<br>[-] | $R^2$<br>[-] | $S_1$<br>[mm] | $\alpha$<br>[-] | $R^2$<br>[-] |
| MS/G          | 123.5         | 0.28            | 0.985        | 55.0          | 8.09            | 1.000        |
| MS/C          | 67.2          | 0.79            | 0.976        | 49.7          | 0.77            | 0.953        |
| GC/G          | 50.0          | 1.78            | 1.000        | 41.5          | 0.56            | 0.991        |
| GC/C          | 90.0          | 0.17            | 0.979        | 33.6          | 0.10            | 0.964        |

Table 6: Parameters for the mean crack spacing Eq.(2), as obtained by data fitting

355 stiffness [59], and the average crack width. The latter strongly affects durability,  
356 for serviceability of structures is endangered by extensive crack opening. Fig.14  
357 illustrates the evolution of the crack spacing, that is the mean spacing between  
358 two adjacent cracks. Data are fitted, as a function of strain, to an exponential  
359 model proposed by Mobasher [2] and successively adopted by Signorini et al.  
360 [52] for durability considerations

$$S(\varepsilon) = S_1 + S_0 \exp[-\alpha(\varepsilon - \varepsilon_1)], \quad \varepsilon \geq \varepsilon_1. \quad (2)$$

361 Here,  $S_1$  represents the saturation value for crack spacing, that is an important  
362 index of interphase strength,  $\varepsilon_1$  is the first strain value in the dataset and  
363  $S(\varepsilon_1) = S_0 + S_1$  the corresponding spacing. The decay parameter  $\alpha$  and the  
364 characteristic saturation mean crack spacing  $S_1$  are fitted for each group and  
365 reported in Table 6. Better performance is associated to lower saturation crack  
366 distances, implying a diffused crack pattern. Indeed, as already discussed, all  
367 coated groups consistently present several closely-spaced cracks, as opposed to  
368 uncoated specimens for which a few far-spaced cracks appear. Interpretation of  
369 the decaying exponent  $\alpha$ , which indicates the capacity of the laminate to crack  
370 at an early stage, appears more difficult. Indeed,  $\alpha$  appears little changing,  
371 with the noticeable exception of a striking increase occurring for G fabric in MS  
372 mortar. For carbon-based systems, the index is not significantly modified by the  
373 coating, while, for GC/G, a slight reduction is found. Such fluctuations can be  
374 ascribed to the coexistence of several competing cracking mechanisms, also in  
375 the brittle matrix, and to the confining effect of the gripping system in the test

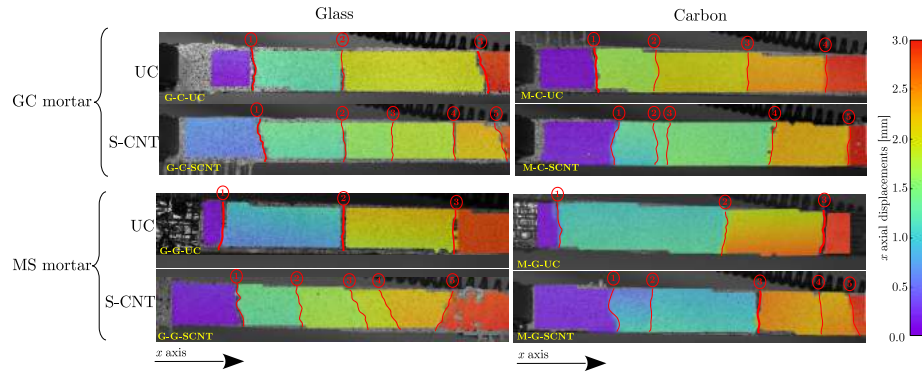


Figure 15: Longitudinal displacement colour map, obtained by DIC post processing, at fixed elongation  $\bar{\epsilon} = 13$  mstrain, for uncoated (upper) and S-CNT coated (lower) TRM specimens

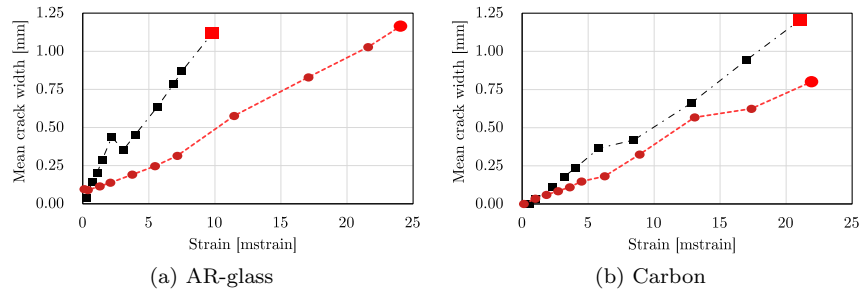


Figure 16: Mean crack width as a function of strain during testing for AR-glass (a) and carbon (b) samples for MS mortar. Uncoated samples are represented by grey dash-dotted lines and square markers, whilst S-CNT specimen behaviour is denoted by circular markers connected by violet dotted lines

376 set-up [60]. Fig.15 presents a colour map description of the displacement field  
 377 in the longitudinal direction and compares coated with uncoated samples at the  
 378 prescribed strain level  $\bar{\epsilon} = 13$  mstrain. The presence of cracks is highlighted  
 379 in red colour. While uncoated specimens present a coarse crack pattern, with  
 380 few large cracks spanning the direction  $y$  orthogonal to the loading, coated  
 381 coupons exhibit a diffused pattern of fine cracks throughout the gauge length.  
 382 This behaviour is directly associated to enhanced adhesion, consistently to the  
 383 findings presented in previous papers and related to plain nano-silica coating  
 384 [51] and to epoxy coating [17].

385 The same pattern is described by Figures 16 and 17, where the evolution  
 386 of the average crack width and of the average crack spacing is presented as a

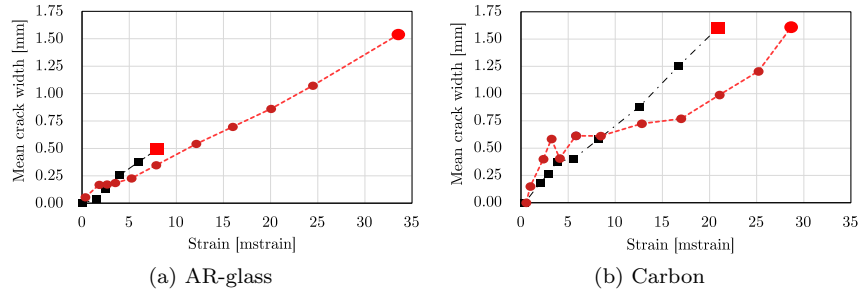


Figure 17: Mean crack width as a function of strain during testing for AR-glass (a) and carbon (b) samples for GC mortar. Uncoated samples are represented with grey dash-dotted lines and square markers, whilst S-CNT ones with violet dotted lines and circular markers.

387 function of strain. Comparing coated and uncoated specimens for any fixed  
 388 value of strain (namely, at the same instant of the test) after the cracking stage,  
 389 the former present lower values than the latter for both indices.

#### 390 4. Conclusions

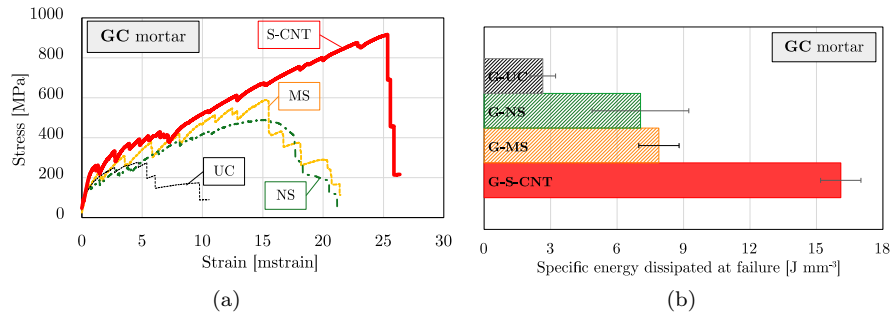


Figure 18: Comparison, in terms of mean strength curves (a) and mean specific energy dissipated at failure (b), for different coating strategies applied to AR-glass in mortar GC: no coating (UC), nanosilica (NS), microsilica (MS) and silica+MWCNTs (S-CNT). Results for microsilica and nanosilica are taken from [21] and [46], respectively

391 We analyse the application of a mineral silica sol-gel coating, loaded with  
 392 dispersed multi-walled carbon nanotubes (MWCNTs), to AR-glass and carbon  
 393 Textile Reinforced Mortar composites for structural purposes. Two inorganic  
 394 lime-based mortars at 56-day curing are considered as embedding medium. Re-  
 395 markable gains in terms of mechanical performance are highlighted in uni-axial  
 396 traction tests, especially with respect to glass fabric. Investigation of the chem-

397 ical adhesion at the fibres-to-matrix interphase, through optical and E-SEM  
398 microscopy, supports the role of the coating in preventing delamination and  
399 telescopic failure. The following conclusions can be drawn:

- 400 • Silica coating takes advantage of pozzolanic reactivity in the neighbour-  
401 hood of the thin mortar layer surrounding the fabric yarns (i.e. the so-  
402 called interphase transition zone) [61];
- 403 • The addition of well-dispersed MWCNTs produces a two-fold increase,  
404 in terms of strength, with respect to the already significant contribution  
405 of plain-vanilla silica coating; thus, an almost optimal performance is at-  
406 tained, that scores slightly below the tensile strength of the dry glass fabric  
407 (i.e. around 1200 MPa);
- 408 • For AR-glass embedded in GC mortar, Fig.18 compares, in terms of  
409 strength curves (a) and specific dissipated energy at failure (b), the present  
410 findings with the outcome of different coating strategies, pertaining to  
411 micro-silica [46] and nano-silica [21] sol-gel. It shows that adding CNTs  
412 roughly double the best outcome both in terms of strength and energy  
413 dissipation;
- 414 • CNTs provide a striking increase in the specific surface area (SSA) of the  
415 reinforcement and effectively roughen its surface. The resulting composite  
416 system exhibits a diffuse crack pattern, with high dissipation capability,  
417 and a prolonged cracking stage associated to several small stress drops in  
418 the strength curve.
- 419 • Coating successfully prevents delamination and telescopic failure, whence  
420 it warrants consistent performance (narrows data scattering), to great  
421 advantage of design limits;
- 422 • Sol-gel coating is especially effective for AR-glass, while mixed results are  
423 retrieved for carbon;



- 424 • Matrix composition strongly affects the overall behaviour, with stronger  
425 binders being, in general, better performing;
- 426 • The inorganic nature of the coating (as opposed to epoxy coating) pre-  
427 serves the attractive features connected to TRM materials.

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#### 437 **Declaration of interest**

438 None

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