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Quiles-Carrillo, L.; Boronat, T.; Montanes, N.; Balart, R.; Torres-Giner, S. (2019). Injection-molded parts of fully bio-based polyamide 1010 strengthened with waste derived slate fibers pretreated with glycidyl- and amino-silane coupling agents. *Polymer Testing*. 77. <https://doi.org/10.1016/j.polymertesting.2019.04.022>



The final publication is available at

<https://doi.org/10.1016/j.polymertesting.2019.04.022>

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Additional Information

1 **Injection-molded parts of fully bio-based polyamide 1010**
2 **strengthened by waste derived slate fibers pre-treated with**
3 **glycidyl- and amino-silane coupling agents**

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13 **Abstract.** Fully bio-based polyamide 1010 (PA1010) was melt-compounded with 15 wt% of slate
14 fibers (SFs), which were obtained from wastes of the tile industry, and the resultant composites were
15 shaped into parts by injection molding. The as-received fibers were first thermally treated and
16 afterwards subjected to surface modification with glycidyl- and amino-silane coupling agents to
17 improve the interfacial adhesion of the composites. The incorporation of both the glycidyl-silane slate
18 fiber (G-SF) and amino-silane slate fiber (A-SF) remarkably improved the mechanical strength of
19 PA1010, inducing a 3-fold increase in tensile modulus. The composite parts prepared with the
20 silanized SFs also presented higher thermal stability and improved thermomechanical resistance.
21 Water uptake was reduced below 1%, encouragingly suggesting that the mechanical performance of
22 the PA1010/SF composites would be scarcely affected by atmospheric humidity. G-SF was the most
23 effective in strengthening PA1010. This improvement was ascribed to the higher reactivity of the
24 cyclic anhydride in the coupled silane with the terminal hydroxyl groups of the biopolymer.

25 **Keywords:** PA1010; environmentally friendly composites; engineering bioplastics; waste
26 valorization

27 **1. Introduction**

28 Polyamides (PAs) are linear and semi-crystalline polymers that are composed of repeating amide
29 groups. PAs are classically petroleum-derived materials though, in the last years, several aliphatic
30 PAs have been obtained partially or totally from bio-based building blocks [1]. Bio-sourced
31 monomers include brassylic acid, sebacic acid, 1,4-diaminobutane (putrescine), and
32 1,5-diaminopentane (cadaverine) [2-4]. Making the properties of the newly so-called bio-based
33 polyamides (bio-PA) similar to those of polyamide 6 (PA6) and polyamide 66 (PA66), for rigid
34 applications, and of polyamide 12 (PA12), for flexible applications, is becoming increasingly
35 important for economical and for sustainable reasons [5]. In particular, the 10-carbon (10C),
36 11-carbon (11C), and 12-carbon (12C) comprising bio-PAs, such as polyamide 610 (PA610),
37 polyamide 1010 (PA1010), polyamide 11 (PA11) or polyamide 1012 (PA1012), have mild and soft
38 physical properties due to their long aliphatic segments, that is, its high methylene-to-amide
39 (CH_2/CONH) ratios, which make them prized for applications that require more flexibility [6]. In this
40 context, recent developments have led to the cost-effective production of bio-based sebacic acid, a
41 C10 dicarboxylic acid derived from castor oil [7]. Sebacic acid can readily react *via* polycondensation
42 with 1,10-decamethylene diamine (DMDA), which can be obtained by exposing sebacic acid to
43 ammonia followed by dehydration and hydrogenation, to produce fully bio-based PA1010 [8].
44 Besides its relatively low melting temperature (T_m), PA1010 is attractive for engineering applications
45 that require high-impact resistance and resilience such as automotive fuel lines, bike tubing, and cable
46 coating [9, 10]. The long alkyl chains of PA1010 also result in a lower water uptake so that their
47 mechanical properties can be less affected by atmospheric humidity [11].

48 Although most bio-PAs show engineering performance, they still have some technical drawbacks
49 related to their tendency to moisture absorption due to the presence of amide groups and relatively
50 low thermomechanical stability. These phenomena are known to have a negative effect on the
51 mechanical and thermal performance of PA-based materials [12]. **Moreover, bio-PAs still present**
52 **higher prices, in the range of US\$15,000–20,000 a ton, than conventional PA6 and PA66, that is,**
53 **US\$2,000–4,000 a ton, or even specialty PA12, that is, US\$8,000–12,000 a ton. The global bio-PA**

54 market demand was approximately 21,000 tons in 2014, which represents around 1% of the
55 worldwide capacity of bioplastics, whereas the growth projection indicates that it is expected to reach
56 over 50,000 tons by 2022 [13]. Fiber reinforcement represents an efficient method to both overcome
57 the above-described technical limitations and reduce cost. Glass fiber (GF) is, with difference, the
58 most used reinforcing filler in PAs [14-17]. Also carbon fiber (CF) and aramid fiber (AF) have being
59 increasingly used for numerous mechanical and tribological applications [18-21]. Nevertheless, the
60 high melt viscosity of PAs together with the chemical inertness of most of these reinforcing elements
61 result in poor matrix–filler interactions that, in turn, are responsible for the performance impairment
62 of the composites [22]. Therefore, surface modification of fibers and/or the use of coupling agents are
63 usually required to enhance the overall performance [18, 23, 24]. In addition, melt grafting of fillers
64 onto polymers is an effective method to achieve compatibilization and, thus, enhance the mechanical
65 strength of composites [25]. For instance, Hui *et al.* [26] reported the usefulness of grafting
66 chemically oxidized CF onto PA6, thus leading to fiber-reinforced composites with increased
67 mechanical properties. Several coupling agents and compatibilizers have been extensively explored
68 to enhance PA–fiber interfacial interactions [27-30]. Among them, silanes and chemically modified
69 silanes are one of the most used coupling agents used in PA-reinforced composites [31].

70 In the last years, some silica-based fibers have been introduced at commercial scale. One of the most
71 promising ones is basalt fiber (BF), which has been proposed in several engineering applications
72 [32-34]. More recently, slate fiber (SF) has also attracted some academic interest as it can be obtained
73 from wastes of the building and construction industry. Slate is a natural rock, typically of a dark grey
74 color, which is widely used in roofs, façades, and for tiling due to its attractive rustic appearance, high
75 wear resistance, and good frost resistance [35]. More than 1 billion tons per year are manufactured in
76 the world, being the Galicia region in northwest Spain one of the largest producers in Europe.
77 However, in spite of the broad use of slate, these manufacturing processes have remained unaltered
78 for many years and are highly inefficient. Indeed, is estimated that more than 90% of the material is
79 wasted during the transformation stages from the quarry up to the final slate tile [36]. As a result, a
80 huge amount of slate wastes is being currently generated in the tile industry. For instance, one ton end
81 product could potentially give 30 tons waste [37]. Estimated price of SF varies from US\$300 to

82 US\$700 a ton, which is comparable or even lower than that of chopped strands of GF. Therefore, not
83 only can this add value to an industrial by-product, but it can also reduce the overall cost of bio-PA
84 articles. However, a limited number of studies have reported so far the use of slate waste as
85 reinforcing filler in thermoplastic matrices. For instance, the incorporation of slate powder into
86 polypropylene (PP) resulted in cost-competitive composites with mechanical and optical properties
87 comparable to neat PP [38]. More recently, new composite laminates based on epoxidized linseed oil
88 (ELO)/SF fabrics were successfully manufactured as alternative to epoxy/GF composites [39]. In
89 another work, it was demonstrated the potential of bio-based high-density polyethylene (bio-HDPE)
90 composites reinforced with short SFs, thus broadening its use for engineering materials [40].

91 This research work aims to develop, for the first time, new environmentally friendly and
92 high-performance composite materials from fully bio-based PA1010 and SF. The use of two different
93 reactive silane coupling agents, that is, a glycidyl- and an amino-silanes, were also investigated in
94 order to modify the fiber surface to improve the biopolymer–fiber interactions and facilitate a better
95 load transfer from the composite components. The mechanical, morphological, thermal, and
96 thermo-mechanical properties as well as water uptake of the newly developed composite parts were
97 evaluated to ascertain their potential in automotive and also building and construction applications.

98 **2. Materials and methods**

99 *2.1. Materials*

100 PA1010 was provided as NP BioPA1010-201 by NaturePlast (Ifs, France). The manufacturer supplies
101 this homopolyamide in pellets as fully bio-based and medium-viscosity grade for injection molding
102 applications. It presents a density of 1.05 g/cm³ and a viscosity number (VN) of 160 cm³/g. A roving
103 of SFs was provided by Mifibra S.L. (Ourense, Spain) obtained from wastes of the tile industry. The
104 monofilaments show a dark brown color, being 4–8 mm in length.

105 A glycidyl-silane, namely (3-glycidyoxypropyl) trimethoxysilane (GPTMS), with CAS number
106 2530-83-8, molecular weight (M_w) of 236.34 g/mol, and density of 1.07 g/cm³, and an amino-silane,
107 namely [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS), with CAS number

108 1760-24-3, M_w of 222.36 g/mol, and density of 1.03 g/cm³, were both purchased at Sigma-Aldrich
109 S.A. (Madrid, Spain). **Figure 1** shows the chemical structures of both silanes.

110 *2.2. Fiber pre-treatment*

111 SFs were first washed extensively with distilled water and then placed in a dehumidifying dryer
112 MDEO from Industrial Marsé (Barcelona, Spain) at 350 °C for 6 h to remove their organic coatings
113 (sizings). The resultant thermally treated fibers were afterwards subjected to surface modification
114 with GPTMS or AEAPTMS to produce, respectively, the here-called silanized slate fiber with
115 glycidyl-silane (G-SF) and amino-silane (A-SF). To this end, both reactive coupling agents were
116 added to distilled water at a concentration of 1 wt%. The fibers were then submerged into the aqueous
117 dissolutions containing each silane and magnetically stirred for 1 h to promote hydrolysis and
118 homogenization. After this, the fibers were extracted from the solution, washed several times with
119 distilled water and, finally, dried at 60 °C for 72 h. A sample of thermally treated slate fiber (TT-SF),
120 without any silane modification, was also obtained as control to compare the effect of silanes on the
121 properties of the composite parts.

122 *2.3. Composite parts preparation*

123 Prior to processing, PA1010 was dried at 60 °C for 36 h in the dehumidifying dryer MDEO to remove
124 any residual moisture. PA1010 and the different SFs were manually pre-homogenized in a zipper bag.
125 In all cases, a fixed weight content of 15 wt-% SF in PA1010 was set. Extrusion was performed using
126 a co-rotating twin-screw extruder from Construcciones Mecánicas Dupra, S.L. (Alicante, Spain),
127 featuring screws of 25 mm diameter with a length-to-diameter ratio (L/D) of 24. The materials were
128 then fed into the main hopper and the rotating speed during extrusion was 20 rpm. The following
129 temperature profile was set: 210 °C (hopper) – 215 °C – 220 °C – 225 °C (die). The PA1010/SF
130 composites were extruded through a round die producing strands that were finally pelletized using an
131 air-knife unit. Residence time was approximately 1 min. **Table 1** gathers the set of compositions
132 melt-processed by twin-screw extrusion.

133 The compounded pellets were dried in the same conditions applied prior to extrusion. Thereafter, they
134 were processed by injection molding using a Meteor 270/75 (Mateu & Solé, Barcelona, Spain). The
135 temperature profile in the injection molding unit was 210 °C (hopper) – 215 °C – 225 °C – 230 °C
136 (injection nozzle). The injected material was shaped in a mold by applying a clamping force of 75
137 tons to obtain the different parts with an average thickness of approximately 4 mm. The cavity filling
138 and cooling times were set to 1 and 10 s, respectively.

139 *2.4. Material characterization*

140 2.4.1. XRF spectroscopy

141 A basic chemical characterization of SF was carried out by X-ray fluorescence (XRF) spectroscopy in
142 a sequential X-ray spectrometer PHILIPS MagiX Pro PW2400 (Amsterdam, The Netherlands). This
143 device was equipped with a rhodium tube and a beryllium window. The chemical composition was
144 analyzed using the SuperQ analytical software (Malvern Panalytical Ltd, Malvern, UK).

145 2.4.2. Morphology

146 The morphology of the SF fillers as well as the fracture surfaces of the PA1010/SF composite parts,
147 which were obtained from the impact tests, was observed by field emission scanning electron
148 microscopy (FESEM). The samples were first sputtered with a gold-palladium alloy in an EMITECH
149 sputter coating SC7620 model from Quorum Technologies, Ltd (East Sussex, UK). Analysis was
150 carried out in a ZEISS ULTRA 55 microscope from Oxford Instruments (Abingdon, UK) using 2 kV
151 as the acceleration voltage.

152 2.4.3. Mechanical tests

153 A universal testing machine ELIB 50 (S.A.E. Ibertest, Madrid, Spain) was used to perform tensile
154 tests on injection-molded dog bone-shaped parts sizing 150 x 10 x 4 mm³. The test was carried out as
155 indicated by ISO 527-1:2012. The cross-head speed was 5 mm/min and the load cell was 5 kN. A
156 676-D durometer (J. Bot Instruments, Barcelona, Spain), using the Shore D-scale, was employed to
157 measure hardness on injection-molded parts with dimensions of 80 x 10 x 4 mm³. The principles of

158 ISO 868:2003 were followed. A 6-J pendulum (Metrotec S.A., San Sebastián, Spain) was employed
159 to determine toughness by the Charpy impact test on injection-molded 0.25-mm V-notched parts with
160 dimensions of 80 x 10 x 4 mm³. The test was done based on the specifications of ISO 179-1:2010. All
161 the mechanical tests were performed at controlled conditions of 25 °C and 40% of relative humidity
162 (RH) for which, at least, 6 samples of each material were evaluated.

163 2.4.4. Thermal analysis

164 A Mettler-Toledo 821 calorimeter (Mettler-Toledo, Schwerzenbach, Switzerland) was employed to
165 analyze the main thermal transitions of the injection-molded PA1010/SF composite parts by
166 differential scanning calorimetry (DSC). Samples with an average weight between 5 mg and 7 mg
167 were placed in standard sealed aluminum crucibles (40 µL). The samples were then subjected to a
168 three stage dynamic thermal cycle at 10 °C/min in a nitrogen atmosphere with a flow-rate of 66
169 mL/min. It consisted of a first heating from 30 °C to 250 °C, followed by cooling to 0 °C, and a
170 second heating to 350 °C. The following equation was used to determine the degree of crystallinity
171 (χ_c):

$$172 \quad \chi_c(\%) = \left[\frac{\Delta H_m}{\Delta H_m^0 \cdot (1-w)} \right] \cdot 100 \quad (1)$$

173 Where ΔH_m (J/g) is the melting enthalpy of the sample, ΔH_{m0} (J/g) = 244 J/g [41] is the theoretical
174 melting enthalpy of a fully crystalline PA1010, and w is the SF weight fraction.

175 A Mettler-Toledo TGA/SDTA 851 thermobalance (Mettler-Toledo, Schwerzenbach, Switzerland)
176 was employed for thermogravimetric analysis (TGA). Samples with an average weight ranging from
177 of 5 mg to 7 mg were placed in standard alumina crucibles (70 µl) and thus subjected to a heating
178 program at 20 °C/min in air atmosphere from 30 °C to 700 °C. The first derivative thermogravimetry
179 (DTG) curves, expressing the weight loss rate as the function of time, were also determined. All
180 thermal tests were carried out in triplicate.

181 2.4.5. Thermomechanical tests

182 A DMA1 dynamic analyzer from Mettler-Toledo was used for dynamical mechanical thermal
183 analysis (DMTA). Tests were performed on injection-molded parts sizing 20 x 6 x 2.7 mm³ in single
184 cantilever flexural conditions. Samples were subjected to a dynamic temperature sweep at 2 °C/min
185 from -60 °C to 160 °C. The selected frequency and maximum flexural deformation or deflection were
186 1 Hz and 10 μm, respectively. All thermomechanical tests were done in triplicate.

187 2.4.6. Water uptake measurements

188 The evolution of water absorption was studied on injection-molded parts of 80 x 10 x 4 mm³ for a
189 whole period of 15 weeks of immersion in distilled water at 24 ± 1 °C. This procedure followed ISO
190 62:2008. Weight measurements were collected weekly in an AG245 analytical balance from
191 Mettler-Toledo with a precision of ± 0.1 mg. Tests were performed in triplicate.

192 3. Results and discussion

193 3.1. Characterization of SF

194 **Table 2** shows a summary of the chemical composition of the as-received SFs obtained by XRF. The
195 results confirmed that SF is mainly constituted by silica (SiO₂). **Figure 2** shows the FESEM images of
196 TT-SF and of the SFs pre-treated with GPTMS and AEAPTMS, respectively called G-SF and A-SF.
197 It can be observed that all the fibers were straight and circular in the cross-section, having a mean
198 diameter in the 5–10 μm range. In **Figure 2a** one can see that the non-silanized fibers, that is, TT-SFs,
199 presented a clean and very smooth surface. This morphology suggests successful removal of any
200 previous sizings during thermal treatment. Further details of the TT-SF morphology are shown in
201 **Figure 2b** in the FESEM image taken at higher magnification. It revealed that the TT-SF surface was
202 not actually smooth but relatively rough based on a wavy morphology with clear steps across the fiber
203 section. In the case of the silane-treated fibers, shown in **Figure 2c** and **Figure 2e** for G-SF and A-SF,
204 respectively, one can clearly observe that the fibers presented the same morphology than TT-SF.
205 However, as seen in the magnified FESEM images shown in **Figure 2d** and **Figure 2f**, the fiber
206 surface became significantly rougher due to the formation of nano-sized precipitates. A similar
207 morphology has been recently reported by Yu et al. [42] for amino-silane-treated BFs during

208 topographical analysis carried out by atomic force microscopy (AFM) analysis. Roughness was
209 ascribed to the presence of spherical silane molecules with radius below 50 nm. One can also observe
210 that the fiber surfaces were also little glossier after silanization, which relates to the formation of thin
211 silane layers that were strongly attached to the SF surface. In this context, it has been reported that
212 layers resulting from the anchorage of silane coupling agents are produced by the formation of a
213 siloxane (Si–O–Si) through reaction between the hydrolyzed alkoxy groups in the silane and
214 hydroxyl functional groups available on the inorganic fibers surface [43]. Coupled silanes can then
215 play a key role in establishing strong interactions among fiber and matrix since, as one can see in
216 previous **Figure 1**, the amino or glycidyl functionality remain still suitable to react with the organic
217 component of the composite.

218 *3.2. Mechanical properties of PA1010/SF composite parts*

219 **Table 3** shows the values of modulus (E), maximum tensile strength (σ_{\max}), and elongation at break
220 (ϵ_b) of the PA1010/SF composite parts obtained from the tensile tests. In relation to the neat PA1010
221 part, E and σ_{\max} were 541 MPa and 56.7 MPa, respectively, while ϵ_b was 622.2%. These mechanical
222 properties indicate that PA1010 generates injection-molded parts with a high ductile behavior but a
223 relatively elasticity. The incorporation of 15 wt% TT-SF into PA1010 induced a significant increase
224 in the mechanical strength of the parts. In particular, E increased to 1560 MPa, that is, nearly a 3-fold
225 increase in comparison to the neat PA1010 part. The value of σ_{\max} also increased up to a value of
226 102.5 MPa, that is, a percentage increase of approximately 81%. In contrast, the ductility was
227 dramatically reduced, showing a ϵ_b value of 14.3%. Similar mechanical changes were reported by
228 Carbonell-Verdú et al. [40], who showed that the incorporation of SF at 20 wt% into bio-HDPE
229 pieces led to a noticeable increase in stiffness, increasing E from 373 MPa to 1483 MPa, and also to a
230 decrease in ductility, reducing ϵ_b from 520% to 18.7%.

231 Both silanized SFs, that is, G-SF and A-SF, positively contributed to further increasing stiffness of the
232 parts without, interestingly, compromising the ductility of the PA1010/TT-SF part. Thus, addition of
233 G-SF led to an increase in E and σ_{\max} to values of 1850 MPa and 111.2 MPa, respectively, while ϵ_b
234 was 13.1%. Similarly, the PA1010/A-SF composite part showed an E value of 1770 MPa, a σ_{\max} of

235 110.4 MPa, and a ϵ_b of 13.4%. Therefore, the mechanical stiffness was slightly higher in the case of
236 the composite prepared with G-SF. In this context, Nishitani et al. [10] showed previously the
237 influence of various silane coupling agents on hemp fiber (HF) that were used to reinforce PA1010. It
238 was demonstrated that the combination of an alkali pre-treatment with sodium hydroxide (NaOH) and
239 a subsequent surface treatment with an ureidosilane was the most effective approach to improve the
240 mechanical strength and hardness of the composite. The effect obtained was mainly attributed to an
241 interfacial interaction improvement between the HF reinforcement element and the PA1010 matrix.
242 Laura et al. [44] also developed PA6-based composites reinforced with GF subjected to previous
243 silanization with different functionalities, that is, amino, epoxy, and anhydride. Authors concluded
244 that the epoxy- and anhydride-silanized GFs offer the optimal mechanical performance, which is also
245 thought to occur due to the highest interfacial interaction between GF and PA6.

246 With regards to the Shore D hardness values, all the tested SFs offered a similar increase. Hardness
247 values increased from 74.8, for the neat PA1010 part, up to values around 80, for the PA1010/SF
248 composite parts. This increase is directly related to the intrinsic hardness of SF. It should be noted that
249 the here-prepared SF-reinforced PA1010 composites are still softer than that of GF-reinforced ones
250 [45], which has the advantage of reducing the wear of the extruder screws. Regarding impact strength,
251 which gives a measurement of the material toughness, both PA1010/SF composite parts produced
252 with the silanized SFs showed intermediate values between the neat PA1010 part and the
253 PA1010/TT-SF composite part. In particular, one can observe that the impact strength was reduced
254 from 10.9 kJ/m², for the neat bio-PA part, to 8.9 kJ/m², for the PA1010/TT-SF composite part. Since
255 impact strength is related to both mechanical ductile and resistant properties, it is considered that the
256 addition of SFs led to a remarkable decrease in elongation at break (ductile property) but, in contrast,
257 improved noticeably the tensile strength, which then further confirms the reinforcing effect of SF. In
258 addition, the efficiency of the silanization on the SF surface and their positive effect on the
259 biopolymer–fiber interactions were evidenced by the fact that the impact-strength values of both the
260 PA1010/G-SF and PA1010/A-SF composite parts were 9.8 kJ/m². Similarly, Samper et al. [39]
261 showed that the impact-strength energy for composites prepared with untreated SF was 66.0 kJ/m²
262 whereas equivalent composite laminates with G-SF presented an absorbed energy of 77.9 kJ/m², that

263 is, 18% higher. This enhancement is, therefore, representative of a good fiber–matrix interaction that
264 allows good load transfer from the matrix to fiber.

265 *3.3. Morphology of PA1010/SF composite parts*

266 **Figure 3** shows the FESEM images corresponding to the fracture surfaces of the injection-molded
267 parts after the impact test. **Figures 3a** and **3b** present the fracture surfaces of the neat PA1010 part
268 taken at 500x and 1000x, respectively. One can observe that the fracture surface was relatively
269 smooth, with several crack fronts, typical of a brittle material. The low plastic deformation observed,
270 however, can be related to the impact test conditions and the use of V-notched parts [46]. **Figure 3c**
271 and **3d** show the FESEM images corresponding to the fracture surfaces of the PA1010/TT-SF
272 composite pieces. It can be observed that TT-SF presented a relatively poor interaction with the
273 PA1010 matrix, which was evidenced by the presence of several holes. The formation of holes and
274 voids indicates that some fibers were pulled out during fracture. In this context, Carbonell-Verdu et
275 al. [40] showed similar fracture surfaces that were ascribed to the absence or poor fiber–matrix
276 interactions between bio-HDPE and SFs. As it can be seen in **Figures 3e** and **3f**, the use of SF
277 pre-treated with glycidyl silane, the so-called G-SF, successfully modified the morphology of the
278 fracture surfaces of the resultant composite parts. Although some cavities and holes were still visible,
279 due to the pulled-out phenomenon described above, they became less intense and the polymer–fiber
280 interaction was also stronger. In fact, in the magnified FESEM image one can observe that the fibers
281 were intensely attached to the biopolymer matrix as an indication of good interaction. Incorporation
282 of the pre-treated SFs with amino-silane, that is, A-SF, yielded similar biopolymer–fiber interaction.
283 This can be evidenced in **Figures 3g** and **3h**, where the number of cavities/holes was reduced and the
284 fibers were highly adhered to the biopolymer matrix.

285 Thus, silanes successfully acted as coupling agents and provided an effective bridge between the
286 inorganic fibers and the PA1010 matrix. In this sense, the use of silanes has given excellent results for
287 different composite materials by improving significantly the interfacial adhesion between inorganic
288 and/or organic fibers and different thermoplastics and thermosets in composite materials. For
289 instance, as reported by Xie et al. [47], the organo-functionality of silane can effectively interact with

290 the polymer matrix depending on the polymer chemistry. Briefly, a non-reactive alkyl group in a
291 silane coupling agent may increase the compatibility with non-polar matrices due to their similar
292 polarities. In other cases, specific reactive organo-functionalities (amino, mercapto, glycidoxy, vinyl,
293 or methacryloxy groups, etc.) in silane can react with some chemical groups of the polymer chains to
294 form newly covalent bonds or, at least, to favor certain interaction between them. Therefore, the
295 functional groups of silanes can respond selectively to the chemical structure of the base resin. In this
296 study, the coupling mechanism of glycidyl-silane is proposed to occur based on the two-step reaction
297 scheme described recently by Samper et al. [43] for epoxy resins. Briefly, in a first stage, the cyclic
298 anhydride would react with the terminal hydroxyl groups ($-OH$) of PA1010, opening the cyclic
299 anhydride and leading to formation of a free carboxylic acid group ($-COO$) that, thereafter, can
300 further react with more available cyclic anhydride rings to form new carboxylic groups. On the other
301 hand, amino-silanes have been reported to successfully act as coupling agents in PA1010 by forming
302 strong intramolecular hydrogen interactions with its amide ($-CONH-$) groups [42]. Based on the two
303 coupling mechanisms reported earlier, one can consider that the effect of glycidyl-silane on bio-PAs
304 is more intense than that of the amino-silane. The first approach implies the formation of newly
305 covalent bonds whereas the latter depends on intramolecular interactions. This dissimilar coupling
306 mechanism can potentially explain the slightly different mechanical performance observed above.

307 *3.4. Thermal properties of PA1010/SF composite parts*

308 **Figure 4** shows the DSC thermograms during the second heating step of the neat PA1010 and
309 PA1010/SF composites. **Table 4** gathers the main thermal parameters obtained from DSC. The
310 heating thermogram was plotted in the 100–250 °C range in order to better elucidate the melting
311 profile of the samples since glass transition of PA1010 is known to be very subtle [11]. It can be
312 observed that the neat PA1010 sample did not show any cold crystallization peak before melting. One
313 can also observe that PA1010 showed a T_m value nearly at 202 °C, melting in a single peak. The value
314 of T_m was slightly reduced by 1–2 °C after the addition of all types of SF. More interestingly, the
315 biopolymer developed a double-melting peak, showing a first melting point around 191 °C, which is
316 characteristic of the well-known phenomenon of melt recrystallization during heating [48]. Briefly,

317 the first peak is due to melting of the polymer fraction that crystallized previously, during cooling or
318 cold crystallization, whereas in the second peak contributes the melting of the recrystallized polymer
319 fraction during heating. In this context, Zhang et al. [49] indicated that the incorporation of
320 montmorillonite (MMT) can restrict the crystallization of PA1010, shifting T_m to lower values. Also,
321 the physical hindrance of silicate layers affected the second melting peak more than the first one.
322 Therefore, one can consider that the presence of SF slightly disrupted the chain-folding process of the
323 biopolymer. This effect can be attributed to segmental immobilization of the biopolymer chains at the
324 fiber surface, which induced a double-melting behavior since the PA1010 chains were more restricted
325 and difficult to recrystallize into thickened, perfect, and stable crystals. A similar observation was
326 also reported by Zeng et al. [50] who showed that the T_m values of PA1010 decreased uniformly with
327 increasing the multi-walled carbon nanotubes (MWCNTs) content. In particular, the highest
328 temperature peak decreased with increasing MWCNTs content and disappeared when the content
329 reached 30 wt%, implying that the movement and re-arrangement of the PA1010 chains were
330 completely restricted in the composites with high MWCNTs loadings. Neat PA1010 was also
331 characterized by a χ_c value of 18%, which is related to its symmetrical chain structure in which the
332 diamine and the dicarboxylic acid are both based on a C10 carbon chain [11]. This structure
333 potentially results in a high regular spacing of the amide groups along the biopolymer chains that, in
334 turn, favors the formation of ordered regions. One can observe that the incorporation of SF slightly
335 increased the percentage of crystallinity of PA1010 up to values in the 18–22% range. This
336 observation suggests that the fibers nucleated the formation of more crystals though less perfect due
337 to the above-described molecular restriction. Similar results have been reported by Mittal et al. [51]
338 who described a significant ΔH_m increase in PA with the graphene addition.

339 TGA curves are plotted in **Figure 5** and the most relevant properties obtained from the curves are
340 listed in **Table 5**. This shows that $T_{5\%}$, which corresponds to the characteristic temperature for a
341 weight loss of 5% and reflects the thermal degradation onset, of the neat PA1010 part was 410.3 °C
342 whereas T_{deg} , determined at the maximum weight loss rate, was located at 473.5 °C. It is also worthy
343 to note that no residual moisture was observed as there was not any significant weight loss in the
344 100–150 °C range. Similar thermal degradation profiles in bio-PAs have been previously described

345 [52, 53]. It has been reported that PA1010 degradation involves a β -C-H transfer reaction
346 mechanism, producing ketoamides as the primary decomposition products [11]. In relation to the
347 composite parts, addition of all types of SF yielded a slight increase in both $T_{5\%}$ and T_{deg} of 2–8 °C
348 and 8–10 °C, respectively. In particular, the PA1010/G-SF composite presented the highest thermal
349 stability, showing a T_{deg} value of 483.1 °C. This increase can be related mainly to a mass transport
350 barrier exerted by the inorganic filler to the volatiles produced during the polymer decomposition
351 [54]. The higher thermal improvement observed for the composites prepared with the silanized fibers
352 can be ascribed to the higher material's cohesion achieved by the silane pre-treatment on the fibers,
353 which enhanced the overall thermal stability of PA1010 in the composites. In this sense, Shen et al.
354 [55] demonstrated that the addition of MWCNTs improves the thermal stability of PA6 by a free
355 radical scavenging effect of the fillers. Then, organic groups in silanes can also potentially contribute
356 to delaying chain cleavage and radical formation during thermal degradation of PA1010. It also
357 worthy to mention that the composites prepared with TT-SF showed a minor mass loss (of
358 approximately 5%) at a temperature below 200 °C. This observation may indicate the presence of
359 some residual water and/or volatiles in the non-silanized SF even though the fibers were subjected to
360 a long thermal pre-treatment. Interestingly, this mass loss was not observed in the composites
361 prepared with G-SF and A-SF, suggesting that a more effective moisture removal was also
362 accomplished during silanization. With regards to the residual mass, all composite samples showed
363 residues of around 15–17% due to the inorganic nature of SF.

364 *3.5. Thermomechanical properties of PA1010/SF composite parts*

365 **Figure 6** shows the DMTA curves of the neat PA1010 and the PA1010/SF composite parts. **Table 6**
366 summarizes some of the thermomechanical properties obtained from the curves. In **Figure 6a** one can
367 observe the evolution of the storage modulus (E') as a function of temperature. The dynamic
368 thermomechanical behavior of PA1010 was characterized by an E' value in the range of 700–825
369 MPa from -50 °C to 25 °C. In the temperature range comprised between 30 °C and 60 °C, the storage
370 modulus decreased progressively down to values of 100–200 MPa. This drop in mechanical stiffness
371 is attributed to the alpha (α)-transition region of PA1010 in which the amorphous phase of the

372 biopolymer changes from the glassy to rubbery state. The composite parts showed a similar evolution
373 of E' with temperature than that observed for the neat PA1010 part, however the samples presented
374 considerably higher values in the whole temperature range. This stiffness increase was more evident
375 below the α -transition region, where E' reached values over 1500 MPa, that is, it was multiplied by a
376 factor two compared to the unfilled biopolymer part. In addition, E' reached values above 600 MPa at
377 90 °C. The thermomechanical enhancement observed was more intense in the composite parts
378 prepared with the silanized fibers. The PA1010/G-SF composite part presented the highest E' value at
379 temperatures below the α -transition region, reaching a value 1685 MPa at 0 °C, whereas the
380 PA1010/A-SF composite part showed similar but slightly lower values above this region. These
381 results are in agreement with the above-described mechanical characterization, performed at room
382 temperature, which showed that the incorporation of SF resulted in a rigidity increase. The further
383 improvement of the mechanical resistant properties for the PA1010/G-SF and PA1010/A-SF
384 composite parts can be attributed to the adhesion increase between fibers and matrix at the interface,
385 as also observed during the morphological analysis. In this regard, Abdelmouleh et al. [56] reported a
386 similar increase in the thermomechanical performance of low-density polyethylene (LDPE) when
387 silane-treated cellulose fibers were incorporated.

388 **Figure 6b** shows the evolution of the damping factor ($\tan \delta$) as a function of temperature. It can be
389 observed that the $\tan \delta$ peak for the neat PA1010 was 51.9 °C. This value is representative of the
390 α -transition of the biopolymer, which relates to its glass transition temperature (T_g). One can observe
391 that the α -peak was slightly shifted to higher temperatures in the PA1010/TT-SF part, that is, 52.7 °C.
392 The shift observed in the composite parts prepared with silanized fibers was also higher, showing
393 values of 54.0 °C and 55.2 °C for PA1010/G-SF and PA1010/A-SF, respectively. The higher T_g
394 values observed for both PA1010/G-SF and PA1010/A-SF composites also confirm the interfacial
395 adhesion improvement achieved by both silane pre-treatments. This supports the previous
396 observation outlined during DSC analysis, indicating that the movement of the biopolymer chains
397 became more restricted and, therefore, the relaxation peak shifted to higher temperatures. It is also
398 worthy to mention the significant reduction of the α -peak values in the composite parts. Since $\tan \delta$
399 represents the ratio between the lost energy (E'') and E' , the lower values observed suggest a lower

400 energy dissipation. This reduction is directly related to the higher E' values due to fiber
401 reinforcement. However, it can also be ascribed partially to the higher crystallinity achieved in the
402 pieces since a reduced percentage of amorphous phase undergoes glass transition [57].

403 3.6. Water uptake of PA1010/SFs composite parts

404 One of the most serious handicap related to the use of fiber-reinforced composites, especially those
405 made of condensation polymers, is their high sensitivity to water that may reduce dramatically their
406 mechanical performance in a damp atmosphere [58]. In general, PAs have high tendency to water
407 absorption due to their relatively high polarity. **Figure 7** shows the evolution of the water uptake of
408 the neat PA1010 part and the PA1010/SF composite parts at room temperature. For all the immersed
409 parts, the water absorption was found to increase with immersion time reaching a *plateau* after
410 approximately 7 weeks. Although PA1010 is not extremely prone to moisture due its relatively high
411 CH_2/CONH ratio, the unfilled part absorbed approximately 1.35 wt% of water. This result is slightly
412 higher than that previously observed for profile-extruded PA1010 tubes [11], that is, 1.20 wt%,
413 possibly due to the lower crystallinity attained in the injection-molded parts. For the composite parts,
414 the equilibrium water uptake was positively reduced to values in the 0.9–1.1 wt% range. This effect
415 was also found to slightly depend on the pre-treatment applied to SF. Thus, PA1010 composites
416 containing TT-SF absorbed 0.97 wt% of water whereas the composites based on G-SF and A-SF
417 showed saturation moisture contents of 0.96 wt% and 1.04 wt%, respectively. It seems therefore that,
418 despite the marked hydrophobic character of SFs, fiber adhesion plays a minor role in water uptake
419 and the silanization pre-treatment performed on the fiber surface did not bring about significant
420 reduction in water absorption. The water uptake reduction observed can be also ascribed to the higher
421 crystallinity achieved in the parts since water molecules are absorbed only in the amorphous regions
422 by involving two close amide groups in an accessible region [59]. Indeed, it has been reported that the
423 use of coupling agents can potentially reduce the water absorption of several fiber-based composites,
424 especially in cellulose-based fibers, though they do not provide a long-term performance [60]. In any
425 case, the low water absorption obtained suggests that the mechanical properties of the composite parts
426 will be nearly unaffected by atmospheric humidity.

427 **4. Conclusions**

428 This work shows that industrial waste derived SFs can be effectively used as novel reinforcing
429 elements in fully bio-based PA1010 parts prepared by conventional industrial processes for
430 thermoplastic materials, as it is the case of injection molding. In particular, the here-prepared
431 injection-molded PA1010/SF composite parts presented a 3-fold increase in the tensile modulus
432 whereas the tensile strength was doubled when compared to the unfilled PA1010 part. This approach
433 was further improved by the pre-treatment of the inorganic fibers with coupling agents from silane
434 family. The incorporation of pre-treated SF with glycidyl- and amino-silanes, called G-SF and A-SF,
435 resulted in an additional increase of the mechanical strength and hardness without impairing the
436 ductility and toughness of the PA1010/TT-SF composite. The mechanical improvement achieved was
437 related to an enhanced adhesion at the biopolymer–fiber interface due to the specific reactive
438 organo-functionalities of each silane. The thermal analysis indicated that the presence of SFs slightly
439 increased the sample crystallinity. However, the fibers also confined the motion of the PA1010
440 chains, restricting their chain-folding process so that less perfect crystals with a thinner lamellae
441 thickness were developed. The composite parts containing G-SF and A-SF also presented slightly
442 higher thermal stability and improved thermomechanical resistance. In particular, thermal
443 degradation was improved by up to 10 °C mainly due to an effect of mass transport barrier to the
444 volatiles produced during decomposition offered by the inorganic fibers, which was further improved
445 in the composites prepared with the silanized fibers. Water uptake was also reduced down to values
446 below 1 wt% in the composite parts, though the effect of the silane pre-treatments was relatively low.
447 Although both silane pre-treatments provided a significant improvement in the mechanical and
448 thermal properties of the PA1010/SF composite parts, the use of G-SF generated parts with slightly
449 higher performance. This effect was ascribed to the more effective coupling mechanism of
450 glycidyl-silane with PA1010. From the above, it can be concluded that G-SF constitutes a good
451 alternative to replace GF, commonly used to reinforce PAs in engineering applications, and the
452 resultant biopolymer composite parts can be of interest for the automotive or the building and
453 construction industries. The use of PA1010 and SFs can contribute positively to the development of
454 sustainable polymer technologies by decoupling raw materials to petroleum and also promoting the

455 valorization of industrial wastes. Future works are also under progress to verify whether the
456 glycidyl-silane reactive coupling agent can effectively enhance the interfacial adhesion of other
457 environmentally friendly polymer composites.

458 **5. Acknowledgments**

459 The Ministry of Science, Innovation, and Universities (MICIU) is acknowledged for funding through
460 the MAT2017-84909-C2-2-R and AGL2015-63855-C2-1-R projects. Quiles-Carrillo holds a FPU
461 grant (FPU15/03812) from the Spanish Ministry of Education, Culture, and Sports (MECD) whereas
462 Torres-Giner is recipient of a Juan de la Cierva–Incorporación contract (IJCI-2016-29675) from
463 MICIU.

464 **6. Data availability**

465 The raw/processed data required to reproduce these findings cannot be shared at this time due to
466 technical or time limitations.

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- 629

630 **Figure captions**

631 **Figure 1.** Chemical structure of the silane coupling agents: (a) (3-glycidyoxypropyl)
632 trimethoxysilane (GPTMS); (b) [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS).

633 **Figure 2.** Field emission scanning electron microscopy (FESEM) micrographs of: (a, b)
634 thermally treated slate fiber (TT-SF); (c, d) slate fiber with glycidyl-silane (G-SF); (e, f) slate
635 fiber with amino-silane (A-SF).

636 **Figure 3.** Field emission scanning electron microscopy (FESEM) images of the fracture surfaces
637 of: (a, b) Polyamide 1010 (PA1010); (c, d) PA1010/thermally treated slate fiber (TT-SF); (e, f)
638 PA1010/slate fiber with glycidyl-silane (G-SF); (g, h) PA1010/slate fiber with amino-silane
639 (A-SF).

640 **Figure 4.** Differential scanning calorimetry (DSC) thermograms of polyamide 1010 (PA1010)
641 and its composites with thermally treated slate fiber (TT-SF) and slate fibers with glycidyl-silane
642 (G-SF) and amino-silane (A-SF).

643 **Figure 5.** (a) Thermogravimetric analysis (TGA) and (b) first derivative (DTG) curves of
644 polyamide 1010 (PA1010) and its composites with thermally treated slate fiber (TT-SF) and
645 slate fibers with glycidyl-silane (G-SF) and amino-silane (A-SF).

646 **Figure 6.** (a) Storage modulus (E') and (b) dynamic damping factor ($\tan \delta$) of polyamide 1010
647 (PA1010) and its composites with thermally treated slate fiber (TT-SF) and slate fibers with
648 glycidyl-silane (G-SF) and amino-silane (A-SF).

649 **Figure 7.** Water uptake of polyamide 1010 (PA1010) and its composites with thermally treated
650 slate fiber (TT-SF) and slate fibers with glycidyl-silane (G-SF) and amino-silane (A-SF).

651 **Tables**

652 **Table 1.** Summary of compositions according to the weight content (wt%) of polyamide 1010
653 (PA1010), thermally treated slate fiber (TT-SF), slate fiber with glycidyl-silane (G-SF), and slate
654 fiber with amino-silane (A-SF).

| Code | PA1010 (wt%) | TT-SF (wt%) | G-SF (wt%) | A-SF (wt%) |
|--------------|---------------------|--------------------|-------------------|-------------------|
| PA1010 | 100 | 0 | 0 | 0 |
| PA1010/TT-SF | 85 | 15 | 0 | 0 |
| PA1010/G-SF | 85 | 0 | 15 | 0 |
| PA1010/A-SF | 85 | 0 | 0 | 15 |

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656

657 **Table 2.** Chemical composition of the as-received slate fiber (SF) obtained by X-ray
658 fluorescence (XRF) spectroscopy.

| Constituent | Percentage (wt%) |
|--------------------|-------------------------|
| SiO ₂ | 91.5 ± 2.8 |
| ZnO | 8.5 ± 2.3 |

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660

661 **Table 3.** Summary of the mechanical properties of polyamide 1010 (PA1010) and its composites
 662 with thermally treated slate fiber (TT-SF) and slate fibers with glycidyl-silane (G-SF) and
 663 amino-silane (A-SF) in terms of tensile modulus (E), maximum tensile strength (σ_{\max}),
 664 elongation at break (ϵ_b), Shore D hardness, and impact strength.

| Parts | E (MPa) | σ_{\max} (MPa) | ϵ_b (%) | Shore D hardness | Impact strength (kJ/m²) |
|--------------|----------------|---|------------------------------------|-----------------------------|---|
| PA1010 | 541 ± 12 | 56.7 ± 1.3 | 622.2 ± 18.5 | 74.8 ± 1.1 | 10.9 ± 0.2 |
| PA1010/TT-SF | 1560 ± 31 | 102.5 ± 1.2 | 14.3 ± 0.4 | 79.8 ± 0.8 | 8.9 ± 0.4 |
| PA1010/G-SF | 1850 ± 63 | 111.2 ± 1.4 | 13.1 ± 0.8 | 79.6 ± 0.5 | 9.8 ± 0.1 |
| PA1010/A-SF | 1770 ± 48 | 110.4 ± 1.9 | 13.4 ± 0.5 | 80.0 ± 0.7 | 9.8 ± 0.5 |

665

666

667 **Table 4.** Main thermal parameters of polyamide 1010 (PA1010) and its composites with
 668 thermally treated slate fiber (TT-SF) and slate fibers with glycidyl-silane (G-SF) and
 669 amino-silane (A-SF) in terms of melting temperature (T_m), normalized melting enthalpy (ΔH_m),
 670 and percentage of crystallinity (χ_c).

| Parts | T_m (°C) | ΔH_m (J/g) | χ_c (%) |
|--------------|---------------------------|--------------------|--------------|
| PA1010 | 202.4 ± 1.0 | 43.9 ± 0.4 | 18.0 ± 0.2 |
| PA1010/TT-SF | 190.9 ± 0.8 / 201.5 ± 1.1 | 43.2 ± 0.5 | 20.8 ± 0.3 |
| PA1010/G-SF | 191.4 ± 1.1 / 201.1 ± 0.9 | 46.9 ± 0.7 | 22.6 ± 0.4 |
| PA1010/A-SF | 191.5 ± 0.9 / 200.8 ± 0.8 | 45.3 ± 0.6 | 21.8 ± 0.3 |

671

672

673 **Table 5.** Main thermal degradation parameters of polyamide 1010 (PA1010) and its composites
674 with thermally treated slate fiber (TT-SF) and slate fibers with glycidyl-silane (G-SF) and
675 amino-silane (A-SF) in terms of temperature at mass loss of 5% ($T_{5\%}$), degradation temperature
676 (T_{deg}), and residual mass at 700 °C.

| Parts | $T_{5\%}$ (°C) | T_{deg} (°C) | Residual mass (%) |
|--------------|----------------------------------|----------------------------------|--------------------------|
| PA1010 | 410.3 ± 0.8 | 473.5 ± 1.0 | 0.3 ± 0.1 |
| PA1010/TT-SF | 411.9 ± 0.9 | 480.3 ± 1.1 | 16.7 ± 0.3 |
| PA1010/G-SF | 417.6 ± 1.1 | 483.1 ± 0.9 | 15.1 ± 0.4 |
| PA1010/A-SF | 418.4 ± 0.9 | 480.5 ± 0.8 | 15.4 ± 0.3 |

677

678

679 **Table 6.** Main thermomechanical parameters of polyamide 1010 (PA1010) and its composites
 680 with thermally treated slate fiber (TT-SF) and slate fibers with glycidyl-silane (G-SF) and
 681 amino-silane (A-SF) in terms of storage modulus (E') measured at 0°C and 90 °C and glass
 682 transition temperature (T_g).

| Parts | E (MPa) at 0 °C | E (MPa) at 90 °C | T_g (°C) |
|--------------|-----------------|------------------|------------|
| PA1010 | 759 ± 20 | 146.2 ± 2.3 | 51.9 ± 0.9 |
| PA1010/TT-SF | 1523 ± 22 | 609.1 ± 2.3 | 52.7 ± 0.7 |
| PA1010/G-SF | 1685 ± 16 | 688.4 ± 1.2 | 54.0 ± 0.8 |
| PA1010/A-SF | 1618 ± 17 | 725.3 ± 1.4 | 55.2 ± 1.1 |

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