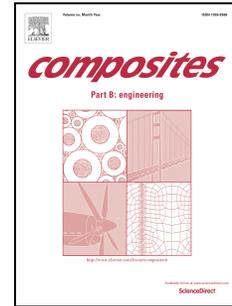


Accepted Manuscript

Behavior of the interphase of dyed cotton residue flocks reinforced polypropylene composites

A. Serra, Q. Tarrés, J. Claramunt, P. Mutjé, M. Ardanuy, F.X. Espinach



PII: S1359-8368(17)31383-5

DOI: [10.1016/j.compositesb.2017.07.015](https://doi.org/10.1016/j.compositesb.2017.07.015)

Reference: JCOMB 5150

To appear in: *Composites Part B*

Received Date: 20 April 2017

Revised Date: 26 June 2017

Accepted Date: 13 July 2017

Please cite this article as: Serra A, Tarrés Q, Claramunt J, Mutjé P, Ardanuy M, Espinach FX, Behavior of the interphase of dyed cotton residue flocks reinforced polypropylene composites, *Composites Part B* (2017), doi: 10.1016/j.compositesb.2017.07.015.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Behavior of the interphase of dyed cotton residue flocks reinforced polypropylene composites.

By:

Serra, A^a, Tarrés, Q^a, Claramunt, J^b, Mutjé, P^a, Ardanuy, M^c, Espinach, FX^{d*}.

^a LEPAMAP Group, Department of Chemical Engineering, University of Girona, Girona 17071, Spain

^b Agri-Food Engineering and Biotechnology Dept., Polytechnic University of Catalunya, Castelldefels 08860, Spain

^c Materials Science and Metallurgic Engineering Dept., Polytechnic University of Catalunya, Barcelona 08019, Spain

^d Design, Development and Product Innovation, Dept. of Organization, Business, University of Girona, Girona 17071, Spain

* Escola Politecnica Superior. Avda. Lluís Santalo, s/n, 17071 Girona, Spain.

Francisco.espinach@udg.edu, tlf. +34 972 418 920, FAX +34 972 418 399

Abstract

Textile industry produces a high amount of residues that, nowadays, are poorly managed. The majority of such wastes are dumped and landfilled. Among all the textile value chain, cotton yarning factories produce wastes in the shape of fiber flocks, with lengths smaller than 10 mm that prevent their reintroduction in the textiles manufacturing process. Nonetheless, such waste cotton flocks could be used as reinforcement for short fiber mould injected composites. This paper reports on the behavior of the interphase between the cotton flocks and a polypropylene matrix. It was found that the organic dyes present on the cotton flocks seem to affect the quality of the interphase in two ways: on the one hand by increasing the affinity between the cotton fibers and the matrix, and on the other hand by limiting the effect of the coupling agents. Micromechanic models are used to further research the quality of the interphase and the intrinsic properties of the composites.

Keywords: A, Fabrics/textiles, fibres; B, Interphase, Strength; E, Injection molding

1 Introduction

Since the textile industry is generating huge amounts of residues, the increasing environmental consciousness and demands of legislative authorities is driving this sector to look for solutions to deliver the remainders into recycling processes and convert these waste products into valuable byproducts [1, 2]. However, the rate of textile recycling is still relatively low. On average, approximately 10 million tons of textile waste is currently dumped in Europe and America each year. Considering the

44 diversity of fibrous waste and structures, many technologies must work in concert in an
45 integrated industry in order to increase the rate of recycling [3, 4].

46 Textiles represent about 3 wt.% of a household bin. At least 50% of the textiles
47 we throw away are recyclable; however, the proportion of textile wastes reused or
48 recycled annually is only around 25%. Although the majority of textile waste provides
49 from household sources, waste textiles also arise during yarn and fabric manufacture,
50 garment-making processes and from the retail industry. In this sense, textile waste can
51 be classified as either pre-consumer or post-consumer. Pre-consumer textile waste
52 consists of by-product materials from the textile, fiber and cotton industries. Each year
53 750,000 tons of this waste is recycled into new raw materials for the automotive,
54 furniture, mattress, coarse yarn, home furnishings, paper and other industries. Through
55 the efforts of this industry approximately 75% of the pre-consumer textile waste that is
56 generated is diverted from our landfills and recycled. Some post-industrial waste is
57 recycled 'in-house', usually in the yarn and fabric manufacturing sector. The rest, aside
58 from going to landfill or incineration, is sent to merchants [5]. As an example, in Hong
59 Kong, there are 253 tons of textiles through up to landfill daily, and the U.S.
60 Environmental Protection Agency estimates that textile waste supposes nearly 5% of all
61 landfill space. The post-consumer waste goes to jumble sales and charities but more
62 typically are disposed of into the trash and end up in municipal landfills. Together, they
63 provide a vast potential for recovery and recycling, which can provide both
64 environmental and economic benefits.

65 Textile waste in landfill contributes to the formation of 'leachate' (the noxious
66 fluid produced in landfill sites) as it decomposes, which has the potential to contaminate
67 both surface and groundwater sources [6]. Another product of decomposition in landfill
68 is methane gas, which is a major greenhouse gas and a significant contributor to global
69 warming, although it can be used if collected. Textile waste is also incinerated in large
70 quantities, and comes third after plastics and cardboard.

71 In the particular case of cotton based textiles, the process used to prepare the
72 fabrics, generates byproducts in the form of cotton flocks. As can be seen in Figure 1, to
73 produce cotton fabrics, on the first step, cotton fibers are yarned to manufacture high
74 quality yarns. These yarns are the used to manufacture fabrics. The manufacturing
75 process produces a large number of byproducts in the shape of fabric trims. These fabric
76 trims are submitted to a defibration process, obtaining cotton fibers. These fibers are
77 yarned and used for the manufacturing of fabrics that will be used to manufacture

78 denim. Anyhow, the defibration process produces fibers with length under 10mm. Such
79 fibers are unable to be yarned and thus are a byproduct of the process without any value
80 or use for the textile industry. This byproduct has the shape of cotton flocks. Moreover,
81 as the yarns used are previously subjected to dyeing processes, these cotton flocks are
82 composed by dyed fibers.

83 Although a lot of studies about the reinforcement of polypropylene with wood-
84 and non-wood cellulose fibers can be found in the literature, only few of them report the
85 use these cotton flocks byproduct as reinforcement for polypropylene-based composites
86 [7-10]. The use of cotton waste is also limited as reinforcement of other polymers, with
87 few publications in the literature [11].

88 One of the main limitations of the these composites is the maximum wt.% of
89 cotton flocks content due to the flock aggregation without any prior treatment. In this
90 sense, Petrucci et al. [9] use a pretreatment of the flocks with a vinyl-acetate water
91 solution to obtain compressed sheets that are subsequently milled, then mixed with PP
92 in a twin screen extruder and finally injection molded. The maximum amount of fiber
93 introduced in this study was 16 wt.%. Araujo et al. [7] prepared composites with until
94 20 wt.% of reinforcement after dye removal and silanization or acetylation treatment.
95 The composites in this case were mixed in a twin screen extruder and compression
96 molded to form the composites.

97 In this work, waste dyed cotton flocks were used as reinforcement for
98 polypropylene-based composites. The cotton flocks were used without any chemical
99 treatment and only were cut down to ensure their correct individualization and
100 dispersion in the matrix. Composites with 30 and 40 wt.% of waste cotton strands
101 (WCS) were prepared. Percentages of polypropylene functionalized with maleic
102 anhydride (MAPP) ranging from 0 to 8 wt.% were added to the composites to find the
103 highest tensile strengths. The results showed tensile strengths higher than expected for
104 the uncoupled composites. Then, the effect of the dye on the interphase was investigated
105 by preparing composites reinforced with virgin cotton fibers. Additionally, the virgin
106 cotton flocks were chemically analysed. A modified rule of mixtures was used to
107 compute the intrinsic tensile strength of the WCS. Initially a good interphase was
108 hypothesised for all the coupled composites. The intrinsic tensile strength of the dyed
109 strands was found to be noticeably inferior to that of the virgin fibers, indicating a
110 negative effect of the dye on the quality of the interphase. Single fiber tensile tests were
111 carried out to obtain the tensile strength of the WCS. The obtained results were

112 submitted to a Weibull analysis to find the characteristic strength of the WCS. The
113 results were tabulated against the fibers length and it was possible to find the
114 characteristic strength of the WCS used in the composites, after its morphologic
115 analysis. Then, the modified Kelly and Tyson equation was used to define the interfacial
116 shear strength of the interphase and the orientation factor.

117 **2 Materials and methods**

118 **2.1 Materials**

119 The cotton flocks residues, treated with a reactive dye, from textile industry and
120 with not enough length for spinning, were kindly supplied by Fontfilva S. L. (Olot,
121 Girona, Spain). Figure 1 shows the aspect of the provided cotton residue flocks.

122 The polymer matrix used was polypropylene (PP) (Isplen PP090 62M) and was
123 kindly supplied by Repsol-YPF (Tarragona, Spain). In order to improve the
124 compatibility between cotton residues and PP, polypropylene functionalized with
125 maleic anhydride (MAPP) (Epolene G3015), with an acid number of 15 mg KOH/g and
126 Mn of 24800, was used as a coupling agent. This was acquired from Eastman Chemical
127 Products (San Roque, Spain).

128 Sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) was used to remove the dyes from the cotton
129 residues and was provided by Sigma Aldrick (Barcelona, Spain). Decalin
130 (Decahydronaphthalene) was acquired from Fischer Scientific (Madrid, Spain) and had
131 190°C boiling point and 97% purity. This reagent was used to dissolve PP matrix in the
132 fiber extraction from composites. All reactants used for cotton flocks characterization
133 were bought from Scharlau Spain (Barcelona, Spain) and used without further
134 purification.

135 **2.2 Methods**

136 **2.2.1 Composite processing**

137 The cotton residues were cut down to a nominal length of 1 mm using a blade
138 mill in order to obtain a better dispersion in the composite. Then, PP, MAPP and cotton
139 flocks residues were mixed at different wt./wt. ratios in an intensive melt mixer
140 Brabender Plastograph (Brabender, Duisburg, Germany) at 185 °C for 10 min, and at 80
141 rpm, in order to ensure to obtain a well-dispersed material. The blends were cut down to
142 pellets with a particle size in the range of 10 mm using a pelletizer equipped with a set
143 of knives and different grids. The pellets were dried and stored at 80°C for 24h. After

144 that, the composite blends were injection-moulded in a Meteor-40 injection machine
145 (Mateu & Solé, Spain). The machine is equipped with three heating areas working at
146 175, 175 and 190 °C, the highest temperature corresponding to the nozzle. First and
147 second pressures were 120 and 37.5 Kg.cm⁻², respectively. This process allowed
148 acquisition of specimens for mechanical characterization (ASTM D638).

149 **2.2.2 Mechanical characterization**

150 Processed materials were placed in a conditioning chamber (Dycometal) at 23°C
151 and 50% relative humidity during 48 hours, in accordance with ASTM D618, prior to
152 testing. Afterwards, samples were mechanically studied by using a Universal testing
153 machine (instrom TM 1122), fitted with a 5 kN load cell. Tensile specimens were
154 shaped like a dog-bone (of approx. 160x13.3x3.2 mm), according to the ASTM D790
155 standard. Results were obtained from the average of at least 5 samples.

156 **2.2.3 Fiber extraction from composites**

157 Cotton residues were extracted from composites by matrix solubilisation using a
158 Soxhlet apparatus and Decalin as a solvent. Small pieces of composites were cut and
159 placed inside a specific cellulose filter and set into a Soxhlet equipment. A small cotton
160 tab was used to prevent the fibers from getting out of the filtering tube. The fiber
161 extraction was carried out during 24 hours. Afterwards, fibers were rinsed with acetone
162 and then with distilled water in order to remove the solvent residue. Finally the fibers
163 were dried in an oven at 105 °C for 24 hours.

164 **2.2.4 Determination of the fiber length and fiber diameter**

165 Fiber length distribution and fiber diameter of the extracted cotton fibers were
166 characterized by means of a Kajanni analyzer (FS-300). A diluted aqueous suspension
167 (1 wt.% consistency) of fibers was analyzed during 2 to 5 minutes, and the length of the
168 fibers was evaluated considering an amount of individual fibers in the range of 2500 to
169 3000 units. Minimums of two samples were analyzed. The Kajanni analyzer offers
170 complete fiber, fines and shiv morphology characterization, but only the fiber length
171 and fiber diameter distribution were used the present work.

172 The fibers were also measured with a Leica DMR-XA optic microscope with a
173 2µm optical resolution.

174 **2.2.5 Cotton strands characterization**

175 **2.2.5.1 Degree of polymerisation**

176 The degree of polymerisation (DP) of cotton fibers was determined according to
 177 UNE 57-039-92. The viscosimetric average molecular weight was calculated from the
 178 equation $\eta = K \cdot M^a$, where η is the intrinsic viscosity, $K = 2.28$ and $a = 0.76$ [12].

179 **2.2.5.2 The solvent used was a copper (II) ethylenediamine by Scharlau Spain**
 180 **(Barcelona, Spain). Cationic demand**

181 The cationic demand of cotton fiber was determined using a Mütek PCD 04
 182 particle charge detector. First, 0.2 g (dried weight) of cotton fiber was diluted in 15 ml
 183 distilled water. Then 25 ml of cationic polymer polydiallyldimethylammonium chloride
 184 (polyDADMAC) was added to before fiber solution and it was mixed for 5 minutes
 185 with magnetic stirring. After this time the mixture was centrifuged in a Sigma
 186 Laborzentrifugen model 6 K 15 for 90 min at 4,000 rpm. Then, 10 ml of the supernatant
 187 was taken to the Mütek equipment. Anionic polymer (Pes-Na) was then added to the
 188 sample drop by drop with a pipette until the equipment reached 0 mV. The volume of
 189 anionic polymer consumed was used to calculate the cationic demand though:

$$190 \quad CD = \frac{(C_{PD} \cdot V_{PD}) - (C_{AP} \cdot V_{AP})}{W_s} \quad (1)$$

191 where CD is the cationic demand ($\mu\text{eq/l}$), C_{PD} = cationic polymer concentration
 192 (g/l), V_{PD} = used volume of cationic polymer (ml), C_{AP} = anionic polymer concentration
 193 (g/l), V_{AP} = used volume of anionic polymer (ml) and W_s = sample's dry weight (g).

194 **2.2.5.3 Chemical composition**

195 Extractives and lignin of cotton fiber residues were determined following TAPPI
 196 standard methods, T222 om-88 and T223 cm-84, respectively. Cellulose content was
 197 measured according to Wise et al. (1946).

198 .

199 **2.2.5.4 Single fiber tensile test**

200 The tensile strength of the cotton flocks was obtained from the force-
 201 displacement curves, following ASTM D3822-01 standard. The measurement was
 202 conducted using the INSTRON 5500R testing device (supplied by INSTRON,
 203 Cerdanyola del Vallès, Spain) equipped with 5kg force cell. The experiment was
 204 repeated at four different gauge lengths; 25.4, 19.05, 12.7 and 6.35 mm, using cross
 205 speed rates of 2.54, 1.905, 1.27 and 0.635 mm/min, respectively. An amount up to 100
 206 single fibers was tested for each gauge length and the maximum force was evaluated.

207 The diameter of the fibers was determined by optical microscopy. Microscopy images
208 were obtained and the width of the fibers was evaluated as a mean value of 3 measures
209

210 **2.2.5.5 Fiber fading**

211 To remove the dye from the cotton flocks, one dry gram of cotton residues was
212 submerged into a hot Sodium hydrosulphite solution (25 wt.%) for two hours. Then,
213 cotton flocks were water rinsed and dried at 50°C.

214 **3 Results and discussion**

215 When hydrophilic natural fibers, as cotton, are used as reinforcement for a
216 hydrophobic matrix, as PP, the use of coupling agents as MAPP is a common practice
217 to obtain good tensile and flexural strength [13-15]. Consequently, searching the
218 percentage of MAPP against fiber content that renders the best tensile strengths (σ_t^C)
219 was the first step proposed by the authors to obtain competitive composite materials.
220 Figure 2 shows the behavior of the tensile strength of the PP-based composite materials
221 containing 30 and 40 wt.% waste cotton strands (WCS) contents, when increasing
222 contents of MAPP were added to the composite formulation.

223 It was found that adding MAPP increased progressively the tensile strength of
224 the composites besides the reinforcement content. The composites with a 30 wt.% of
225 WCS increased their tensile strength a 57.2, 63.7 and a 70.6% against the matrix when
226 2, 4 and 6% of MAPP was added, respectively. If the same values are compared with
227 the composite without MAPP the respective increases were 13.6, 18.3 and 23.3%.
228 Further MAPP contents caused a drop of the tensile strength of the composite. The most
229 probable cause could be the self-entanglement of the MAPP chains [16]. The
230 composites with a 40 wt.% content of WCS showed a similar behavior, with a
231 maximum observed tensile strength when a 6% of MAPP was added to its formulation.
232 Such MAPP content rendered 94.2 and 28.5% increases of the tensile strength,
233 compared to the matrix and the uncoupled composite, respectively. While the increases
234 against the matrix were found to be significant, the tensile strength of the uncoupled
235 composites was found to be remarkably high [13, 17].

236 The uncoupled composite materials with 30 and 40 wt.% WCS increased the
237 tensile strength of the matrix a 38.4 and a 51.1%, respectively. Such increases are really
238 significant when compared with other uncoupled cellulosic fiber reinforced composites.
239 A probable cause for such behavior could be due to the dye agents affecting surface

240 chemical character of the cotton flocks. In that sense, the cationic demand of the dyed
 241 cotton residue flocks, expressed in micro-equivalents of polyDACMAC per gram of
 242 reinforcement, was estimated at 16.39 $\mu\text{eq. g/g}$, while the virgin cotton fibers showed a
 243 58.7 $\mu\text{eq. g/g}$ demand [18]. The change on the superficial hydrophilicity of the dyed
 244 cotton is significant, increasing its hydrophobicity, and consequently increasing its
 245 affinity with the PP. The effect is similar to that obtained by diminishing the
 246 hydrophilic nature of natural fibers by surface treatment with alkyl ketene dimmer
 247 (AKD) [19, 20]. Then, some cotton residue flocks were faded, and their cationic
 248 demand was measured to be 48.9 $\mu\text{eq. g/g}$. Besides, some dyed and faded flocks were
 249 suspended in a water/hexane mixture (50/50%). Figure 3 shows the result.

250 It was found that the dyed and the faded cotton flocks had affinity with the
 251 organic phase (hexane), and aqueous phase, respectively. Consequently, it was apparent
 252 that the dyeing agents changed the surface character of the cotton fibers, increasing their
 253 hydrophobicity, and consequently their affinity with the PP, and thus resulting in
 254 comparatively high tensile strengths for the uncoupled composites [21].

255 Nonetheless, it is probable that such dyeing agents also affect the interactions of
 256 the cotton fiber surfaces with the MAPP, limiting its strengthening power. To that
 257 effect, a modified Rule of Mixtures (mRoM) was used to analyze the experimental
 258 results (Eq. 1).

$$259 \quad \sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \quad (1)$$

260 Were σ_t^C , σ_t^F and σ_t^{m*} are the tensile strength of the composite, the intrinsic
 261 tensile strength of the strands, and the tensile strength of the matrix at the composites'
 262 failure strain. The value of σ_t^{m*} was computed with a polynomial 4th regression of the
 263 stress strain curve of the matrix (Eq.2).

$$264 \quad \sigma_t^{m*} = -0.0001 \cdot (\varepsilon_t^C)^5 + 0.0014 \cdot (\varepsilon_t^C)^4 + 0.0468 \cdot (\varepsilon_t^C)^3 - 1.1307 \cdot (\varepsilon_t^C)^2 + 9.0559 \cdot \varepsilon_t^C$$

265 (2)

266 V^F is the volume fraction of the reinforcement, and f_c is the coupling factor that
 267 is used to account for the effect of the fiber length and orientation, and the quality of the
 268 interface between the fibers and the matrix. It has been reported that bell bonded semi-
 269 aligned short fiber composites show coupling factor with 0.2 values [17, 22, 23].

270 The mRoM was used to obtain the value of the intrinsic tensile strengths of the
 271 cotton fibers, using the experimental results (Figure 3, Table 1), and a 0.2 coupling
 272 factor, assuming a high quality interphase in the case of the composites containing a 6%
 273 of MAPP.

274 The obtained σ_t^F were 658.2 and 624.5 MPa for the 30 and 40% coupled
275 composites, respectively. Such intrinsic tensile strengths are sensibly higher to
276 previously reported values [24, 25]. Nonetheless, if the dyeing agents affect the
277 interactions between the fiber surface and the MAPP it means that the composites could
278 not be defined as well bonded, and consequently, lower values of the coupling factor
279 were expected. Anyhow, lower values of the coupling factor will produce higher
280 intrinsic tensile strengths (a 0.15 coupling factor renders 1005 MPa intrinsic tensile
281 strength). In the literature there are references to the intrinsic tensile strength of cotton
282 fibers in the range from 287 to 800 MPa [26, 27]. The large variability of such value is
283 common to natural fibers.

284 For comparison purposes, virgin cotton flocks were used to prepare a composite
285 with a 20% of such fibers as reinforcement (the composite was coupled with a 6% of
286 MAPP). Once tensile tested its tensile strength was 46.86 MPa and its strain at break
287 was 4.9%. These new experimental data were used anew to back calculate the
288 correspondent intrinsic tensile strength of virgin cotton flocks, by using the mRoM, and
289 assuming a 0.2 coupling factor, obtaining a 1017.4 MPa value. The dyed and the virgin
290 cotton strands are very similar, being its main difference the presence or not of dyeing
291 agents and consequently its effect on the reactivity between the strands surface and the
292 MAPP. Then, if the intrinsic strength of the cotton flocks is established at a value
293 around 1000 MPa, it is clear that the coupling factor in the case of the dyed cotton
294 strands-based composites is lower than 0.2, and such composites could not considered
295 fully well bonded. It is known that the contribution of a reinforcing fiber to the tensile
296 strength of a composite depends on its intrinsic tensile strength, but also in the nature of
297 the bonds between the matrix and the fibers, and the number of such bonds per volume
298 fraction. These virgin cotton flocks were chemically analyzed (table 2), and their
299 chemical composition and its degree of polymerization (DP) further support high
300 intrinsic tensile strengths for such fibers.

301 It was found that the cellulose and the alpha-cellulose contents, and its degree of
302 polymerization were comparatively very high. A bleached pine Kraft pulp (BPKP)
303 shows lesser cellulose contents (84.1 wt.%, with a 15.9 wt.% of hemicelluloses), and a
304 polymerization degree of 1197. A PP-based composite material reinforced with a 40
305 wt.% of BPKP, coupled with a 6% of MAPP reported that the intrinsic tensile strength
306 of the BPKP is 474.6 MPa. The qualitative and quantitative differences with the cotton

307 fibers are clear. With the objective of clarifying the value of the intrinsic tensile strength
 308 of the cotton flocks single fiber tensile tests were performed.

309 **3.1 Cotton flocks intrinsic mechanical properties.**

310 Figure 4 shows two representative samples of the evaluation of the mean
 311 diameter (width) of the fibers submitted to single fiber tensile test.

312

313 The width of the single fibers was very regular, fiber to fiber, with slight
 314 variation between them. The mean diameter of all the evaluated fibers was 17.35 μm .
 315 Then, the fibers were submitted to tensile test. Figure 5 shows the results of the single
 316 fiber tests against the gauge length.

317 The intrinsic properties of the Cotton fibers were computed after a Weibull
 318 analysis of the single fiber tests experimental results. The Weibull analysis describes the
 319 probability of failure of a fiber under stress. The probability of failure under a given
 320 stress (σ) is directly linked to the presence of a defect in the fiber surface with the size
 321 that allows crack propagation [28]. The failure stress is distributed accordingly to a
 322 Weibull distribution, described by equation 3:

$$323 \quad P_f(\sigma) = 1 - e^{-\left[\left(\frac{\sigma}{\eta}\right)^\beta\right]} \quad (3)$$

324 Where, β is known as the Weibull modulus, and is a measure of the dispersion of
 325 the strength values. The higher the Weibull modulus is, the shorter is the scatter of the
 326 strength values. In the same equation, σ and η are the measured fiber tensile strengths,
 327 and the scale factor or the characteristic strength of the fiber. With the objective of
 328 measuring the intrinsic tensile strength of the fibers the gauge length of the Instron
 329 universal dynamometer were established at four different positions; 1, $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$
 330 inches (25.40, 19.05, 12.70 and 6.35mm). At least 100 fibers were tested for each gauge
 331 lengths. The strength of a fiber is highly dependent on its length, as the higher the
 332 length, higher is the probability of finding a defect. Besides, natural fibers usually show
 333 high standard deviations on their mechanical properties, thus a scatter on their
 334 properties was expected. Upper and lower strength values were omitted in agreement
 335 with the research by Thomason [29].

336 Figure 6 shows the linearized representation of the probability of failure against
 337 the natural logarithm of the measured intrinsic fiber tensile strength.

338 Table 2 shows the experimental mean intrinsic tensile strengths (σ_t^F) and its
 339 standard deviations. As expected the experimental values were higher for the shorter
 340 fibers. For comparison purposes the table also adds the specific mean tensile strengths
 341 of the fibers ($\sigma_t^F, \text{specific}$). In that sense, the specific intrinsic tensile strength of a glass
 342 fiber is around 580 MPa/g cm³, and a flax fiber around 600 MPa/g cm³ [30]. The
 343 Weibull modulus and the characteristic strengths were computed after the statistical
 344 analysis and are also shown in table 3.

345 The low value of the Weibull modulus reflects the exhibited wide scatter. The
 346 measured mean intrinsic tensile strengths are similar to their respective characteristic
 347 strengths. The characteristic strengths also visualize the highest probability of failure for
 348 the longest fibers. Figure 5 shows a linear evolution of the tensile strength of the single
 349 fibers against the gauge length. This gauge length is equivalent to the fiber length and a
 350 linear regression of the intrinsic tensile strength of the fibers (σ_t^F) against its length (L^F)
 351 delivers Eq. 3:

$$352 \quad \sigma_t^F = 952 - 16.504 \cdot L^F \quad (3)$$

353 Usually the mean lengths of the fibers inside the composites show values much
 354 shorter than that of the gauge lengths. The regression equation can be used to compute
 355 the intrinsic tensile strength of the reinforcing fibers, once such fibers are
 356 morphologically characterized. This morphological analysis indicated that the mean
 357 diameter of the fibers was 16.5 μm . Figure 7 shows the length distribution of the cotton
 358 fibers extracted from the matrix, for the case of the coupled composite with a 40% of
 359 WCS.

360 It was found that the mean arithmetic lengths of the coupled composites with 30
 361 and 40 wt.% WCS contents were 239 and 210 μm , respectively. In the same way, the
 362 respective single weighted length was 374 and 339 μm . The equation presented with the
 363 figure 5 was used to compute the respective intrinsic tensile strength; obtaining 948.0
 364 and 948.5 MPa values for the 239 and 210 μm mean lengths, respectively. The values
 365 are very similar to those obtained by using the mRoM while assuming a good
 366 interphase. Nonetheless, there are studies that observe notable differences between the
 367 intrinsic tensile strengths of the fibers if a re experimentally measured or back-
 368 computed by using micromechanical models [31].

369 With the morphologic data of the reinforcing fibers and the results of the tensile
 370 tests of the matrix and the composites it was possible to use the modified Kelly and
 371 Tyson model [32-34] (Eq. 4) to assess the quality of the interphase.

372

$$373 \quad \sigma_t^c = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^F \cdot V_i^F}{d^F} \right] + \sum_j \left[\sigma_t^F \cdot V_j^F \left(1 - \frac{\sigma_t^F \cdot d^F}{4 \cdot \tau \cdot l_j^F} \right) \right] \right) + (1 - V^F) \cdot \sigma_t^{m*} \quad (4)$$

374

375

376

377

378

379

In Equation 4 the d^F and l_{ij}^F terms represent the fiber diameter and length, respectively. χ_1 is the orientation factor, modifying the original Kelly and Tyson model, developed for aligned reinforcements. Finally, τ is the interfacial shear strength, accounting for the ability of the interphase to transmit loads from the matrix to the fiber [35].

380

381

382

383

384

385

386

387

388

Previous works found that the orientation angle was highly influenced by the machinery used during the mould injection of the specimens. It was found that such parameter also rendered values between 0.25 and 0.35. It is accepted that the relation between the orientation factor and the mean orientation angle (α) is represented by: $\alpha = \cos^4(\chi_1)$. Accordingly, the mean orientation angles were between 40 and 45°. It is also known that Von Mises criteria: $\tau = \sigma_t^c / 3^{1/2}$ could be used to predict the value of the interfacial shear strength in the case of very good interphases, and also an upper bound for such value (cites). As the used PP had an tensile strength of 27.6 MPa, Von Mises criteria establishes a 15.9 MPa value for τ .

389

390

391

392

393

394

395

396

397

398

399

400

401

402

403

404

A numerical solution for the Kelly and Tyson equation was proposed in order to know the value of the interfacial shear strength and the orientation factor for the composites that added a 6% of MAPP. If the equation is handled individually for both composites shows two incognita, being impossible to solve. On the other hand it is wise thinking that both values will be similar for the composites with a 40 and 30% of cotton fiber reinforcement, being the case in previous researches [17, 23]. Thus, a numerical iterative method was applied to find a value for the interfacial shear strength and the orientation factor for both composites that showed the lowest distance between the computed values. The initialization values were a 0.3 orientation factor and 16 MPa interfacial shear strength. The method converged very fast to interfacial shear strengths around 14.8 MPa and an orientation factors in the range from 0.33 to 0.34. The interfacial shear strength was inferior to Von Mises, showing that the interphase has possibilities to be improved, supporting that the dye somehow limited the interaction between the fibers and the polymer. At the same time, the orientation factor was inside the 0.25 to 0.35 range found in previous works [14, 17]. Besides the value coincides with the mean value of the orientation factor predicted by other researchers [36]. The

405 orientation factor was used to compute the theoretical interfacial shear strength of the
406 uncoupled composites, obtaining 6.5 and 8.3 MPa values for the 30 and 40%
407 composites, respectively. Such values are in line with those shown by other natural fiber
408 reinforced polypropylene composites [17, 23].

409 Finally, the mRoM (Eq.1) was used to compute the value of the coupling factor
410 of the coupled and uncoupled WCS-based composites. The coupled composites with 30
411 and 40 wt.% WCS contents rendered 0.159 and 0.146 coupling factor values,
412 respectively. The value is far from 0.2, pointing out improvable interphases, and further
413 adding to the negative effect of the dyes on such interphases. On the other hand, the
414 same uncoupled composites showed coupling 0.117 and 0.105 coupling factors,
415 respectively. Such values are high in comparison with other natural fiber uncoupled
416 composites, which show slightly positive values [13, 23, 37, 38].

417 **4 Conclusions**

418 A by-product of the textile industry in the shape of waste cotton flocks was used
419 to reinforce polypropylene. This use could inertize such by-product and extend the
420 value chain of the textile industries.

421 It was found that the organic dyes favored the interphase between the cotton
422 flocks and the matrix, as long as their composite materials showed comparatively
423 relevant tensile strength, without any coupling agent. At the same time, it was apparent
424 that the aforementioned dyes affected negatively the action of the coupling agents.

425 The tested cotton flocks presented intrinsic tensile strengths superior to that
426 found in the bibliography. With such strengths, its composites could replace glass fiber-
427 based reinforced composites.

428 The intrinsic tensile strengths of the cotton flocks were obtained by single fiber
429 tensile test, and as it is known that the fibers suffer morphologic changes when
430 composed. Thus, it is probable that its intrinsic tensile strength inside the composite is
431 different to that outside. A more accurate micro-mechanics analysis could unveil
432 possible deviations from the experimental values.

433 The interfacial tensile strength and the orientation factor obtained in the analysis
434 are consistent with the literature.

435

436 **References**

437

- 438 [1] Mishra R, Behera B, Militky J. Recycling of Textile Waste Into Green Composites:
439 Performance Characterization. *Polymer Composites*. 2014;35(10):1960-7.
- 440 [2] DeVallance DB, Gray J, Lentz H. PROPERTIES OF WOOD/RECYCLED TEXTILE
441 COMPOSITE PANELS. *Wood Fiber Sci*. 2012;44(3):310-8.
- 442 [3] Mulinari DR, Voorwald HJC, Cioffi MOH, Lima CAA, Baptista C, Rocha GJM.
443 Composite materials obtained from textile fiber residue. *Journal of Composite*
444 *Materials*. 2011;45(5):543-7.
- 445 [4] Barbero-Barrera MdM, Pombo O, Navacerrada MdlÁ. Textile fibre waste
446 bindered with natural hydraulic lime. *Composites Part B: Engineering*. 2016;94:26-
447 33.
- 448 [5] Ryu C, Phan AN, Sharifi VN, Swithenbank J. Combustion of textile residues in a
449 packed bed. *Exp Therm Fluid Sci*. 2007;31(8):887-95.
- 450 [6] Jha MK, Kumar V, Maharaj L, Singh RJ. Studies on leaching and recycling of zinc
451 from rayon waste sludge. *Industrial & Engineering Chemistry Research*.
452 2004;43(5):1284-95.
- 453 [7] Araújo RS, Rezende CC, Marques MF, Ferreira LC, Russo P, Emanuela Errico M,
454 et al. Polypropylene - based composites reinforced with textile wastes. *J Appl*
455 *Polym Sci*. 2017.
- 456 [8] Haque MS. Processing and characterization of waste denim fiber reinforced
457 polymer composites. 2014.
- 458 [9] Petrucci R, Nisini E, Puglia D, Sarasini F, Rallini M, Santulli C, et al. Tensile and
459 fatigue characterisation of textile cotton waste/polypropylene laminates.
460 *Composites Part B: Engineering*. 2015;81:84-90.
- 461 [10] Taşdemir M, Koçak D, Usta I, Akalin M, Merdan N. Properties of polypropylene
462 composite produced with silk and cotton fiber waste as reinforcement.
463 *International Journal of Polymeric Materials*. 2007;56(12):1155-65.
- 464 [11] Tserki V, Matzinos P, Panayiotou C. Effect of compatibilization on the
465 performance of biodegradable composites using cotton fiber waste as filler. *J Appl*
466 *Polym Sci*. 2003;88(7):1825-35.
- 467 [12] Henriksson M, Berglund LA, Isaksson P, Lindstrom T, Nishino T. Cellulose
468 nanopaper structures of high toughness. *Biomacromolecules*. 2008;9(6):1579-85.
- 469 [13] Reixach R, Espinach FX, Arbat G, Julián F, Delgado-Aguilar M, Puig J, et al.
470 Tensile Properties of Polypropylene Composites Reinforced with Mechanical,
471 Thermomechanical, and Chemi-Thermomechanical Pulps from Orange Pruning.
472 *BioResources*. 2015;10(3):4544-56.
- 473 [14] Granda LA, Espinach FX, Lopez F, Garcia JC, Delgado-Aguilar M, Mutje P.
474 Semichemical fibres of *Leucaena collinsii* reinforced polypropylene:
475 Macromechanical and micromechanical analysis. *Compos Pt B-Eng*. 2016;91:384-
476 91.
- 477 [15] Li Y, Pickering KL, Farrell RL. Determination of interfacial shear strength of
478 white rot fungi treated hemp fibre reinforced polypropylene. *Composites Science*
479 *and Technology*. 2009;69(7-8):1165-71.
- 480 [16] Beckermann GW, Pickering KL. Engineering and evaluation of hemp fibre
481 reinforced polypropylene composites: Micro-mechanics and strength prediction
482 modelling. *Composites Part A-Applied Science and Manufacturing*.
483 2009;40(2):210-7.

- 484 [17] Vallejos ME, Espinach FX, Julian F, Torres L, Vilaseca F, Mutje P.
485 Micromechanics of hemp strands in polypropylene composites. *Composites*
486 *Science and Technology*. 2012;72(10):1209-13.
- 487 [18] Carrasco F, Mutjé P, Pelach MA. Control of retention in paper-making by
488 colloid titration and zeta potential techniques. *Wood Science and Technology*.
489 1998;32(2):145-55.
- 490 [19] Mutje P, Girones J, Lopez A, Llop MF, Vilaseca F. Hemp strands: PP composites
491 by injection molding: Effect of low cost physico-chemical treatments. *Journal of*
492 *Reinforced Plastics and Composites*. 2006;25(3):313-27.
- 493 [20] Vilaseca F, Lopez A, Llauro X, Pelach MA, Mutje P. Hemp strands as
494 reinforcement of polystyrene composites. *Chemical Engineering Research &*
495 *Design*. 2004;82(A11):1425-31.
- 496 [21] Zhou Y, Fan M, Chen L. Interface and bonding mechanisms of plant fibre
497 composites: An overview. *Composites Part B: Engineering*. 2016;101:31-45.
- 498 [22] Sanadi AR, Young RA, Clemons C, Rowell RM. Recycled newspaper fibers as
499 reinforcing fillers in thermoplastic: 1 analysis of tensile and impact properties in
500 polypropylene *Journal of Reinforced Plastics and Composites*. 1994;13(1):54-67.
- 501 [23] Reixach R, Franco-Marquès E, El Mansouri N-E, de Cartagena FR, Arbat G,
502 Espinach FX, et al. Micromechanics of Mechanical, Thermomechanical, and Chemi-
503 Thermomechanical Pulp from Orange Tree Pruning as Polypropylene
504 Reinforcement: A Comparative Study. *BioResources*. 2013;8(3).
- 505 [24] Kompella MK, Lambros J. Micromechanical characterization of cellulose fibers.
506 *Polymer Testing*. 2002;21(5):523-30.
- 507 [25] Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres.
508 *Progress in Polymer Science*. 1999;24(2):221-74.
- 509 [26] Yan L, Kasal B, Huang L. A review of recent research on the use of cellulosic
510 fibres, their fibre fabric reinforced cementitious, geo-polymer and polymer
511 composites in civil engineering. *Composites Part B: Engineering*. 2016;92:94-132.
- 512 [27] Kong C, Lee H, Park H. Design and manufacturing of automobile hood using
513 natural composite structure. *Composites Part B: Engineering*. 2016;91:18-26.
- 514 [28] Rösler J, Harders H, Baeker M. Mechanical behaviour of engineering materials:
515 metals, ceramics, polymers, and composites: Springer Science & Business Media;
516 2007.
- 517 [29] Thomason J. On the application of Weibull analysis to experimentally
518 determined single fibre strength distributions. *Composites Science and*
519 *Technology*. 2013;77:74-80.
- 520 [30] Cañigueral N, Vilaseca F, Méndez JA, López JP, Barberà L, Puig J, et al. Behavior
521 of biocomposite materials from flax strands and starch-based biopolymer.
522 *Chemical Engineering Science*. 2009;64(11):2651-8.
- 523 [31] Shah DU, Nag RK, Clifford MJ. Why do we observe significant differences
524 between measured and 'back-calculated' properties of natural fibres? *Cellulose*.
525 2016;23(3):1481-90.
- 526 [32] Kelly A, Tyson W. Tensile properties of fibre-reinforced metals -
527 copper/tungsten and copper/molybdenum. *Journal of the Mechanics and Physics*
528 *of Solids*. 1965;13(6):329-38.
- 529 [33] Espinach FX, Granda LA, Tarrés Q, Duran J, Fullana-i-Palmer P, Mutjé P.
530 Mechanical and micromechanical tensile strength of eucalyptus bleached fibers
531 reinforced polyoxymethylene composites. *Composites Part B: Engineering*.
532 2017;116:333-9.

- 533 [34] Granda LA, Espinach FX, López F, García JC, Delgado-Aguilar M, Mutjé P.
 534 Semichemical fibres of *Leucaena collinsii* reinforced polypropylene:
 535 Macromechanical and micromechanical analysis. *Composites Part B: Engineering*.
 536 2016;91:384-91.
- 537 [35] Serrano A, Espinach FX, Julian F, del Rey R, Mendez JA, Mutje P. Estimation of
 538 the interfacial shears strength, orientation factor and mean equivalent intrinsic
 539 tensile strength in old newspaper fiber / polypropylene composites. *Composites*
 540 *Part B: Engineering*. 2013(50):232-8.
- 541 [36] Fu SY, Lauke B. Effects of fiber length and fiber orientation distributions on
 542 the tensile strength of short-fiber-reinforced polymers. *Composites Science and*
 543 *Technology*. 1996;56(10):1179-90.
- 544 [37] Serrano A, Espinach FX, Tresserras J, del Rey R, Pellicer N, Mutje P. Macro and
 545 micromechanics analysis of short fiber composites stiffness: The case of old
 546 newspaper fibers-polypropylene composites. *Materials & Design*. 2014;55:319-24.
- 547 [38] Lopez JP, Mendez JA, Espinach FX, Julian F, Mutje P, Vilaseca F. Tensile
 548 Strength characteristics of Polypropylene composites reinforced with Stone
 549 Groundwood fibers from Softwood. *BioResources*. 2012;7(3):3188-200.

550

551 **Figure Captions**552 **Figure 1: Cotton textiles manufacturing roadmap.**

553 **Figure 2: Tensile strength of the composites against its MAPP content. (a) Composites with a 30% of**
 554 **cotton strands, (b) composites with a 40% of cotton strands**

555 **Figure 3: Dyed and faded cotton residue suspended in a water/hexane mixture.**556 **Figure 4: Evaluation of the mean diameter of the single cotton fibers.**

557 **Figure 5: Intrinsic tensile strength of the dyed cotton strands submitted to single fiber tensile test,**
 558 **against the gauge length**

559 **Figure 62: Linearized cumulative probability of failure against the natural logarithm of the**
 560 **measured fiber tensile strengths for each gauge length.**

561 **Figure 7: Fiber length distribution of the WCS extracted from the 40% reinforced coupled composite.**

562

563 **Tables**564 **Table 1: Experimental results used to solve the mRoM**

Fiber type	Fiber Content (%)	MAPP (%)	V^f	ϵ_t^C (%)	σ_t^{m*} (Mpa)
WCS	30	0	0.205	3.5	20.0
WCS	40	0	0.287	3.3	19.4
WCS	30	6	0.205	3.9	21.1
WCS	40	6	0.287	3.7	20.6
Virgin cotton	20	6	0.131	4.9	23.2

565

566 **Table 2: Chemical composition of the Surface and degree of polymerization of the virgin cotton strands**

Cellulose	α cellulose	Lignin	Extractives	Ash	Others	D. P.
93.8%	89.95%	0.55%	2.85%	1.15%	1.15%	4727

567

568 **Table 3: Experimental mean intrinsic tensile strengths of the fibers, and the Weibull analysis**569 **outputs.**

Gauge length (mm)	$\sigma_t^f \pm SD$ (MPa)	$\sigma_{t, \text{specific}}^f$ (MPa/g cm ³)	Weibull shape factor β	Characteristic strength η (MPa)
6.35	739 \pm 356	493	2.2	854
12.70	638 \pm 310	425	2.3	735
19.05	540 \pm 273	360	2.4	632
25.40	478 \pm 256	319	2.4	539

570

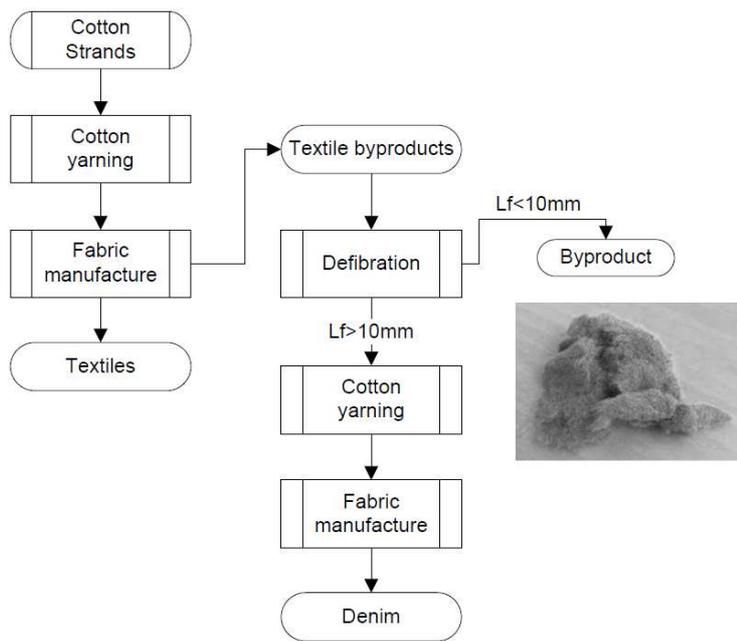


Figure 1: Cotton textiles manufacturing roadmap.

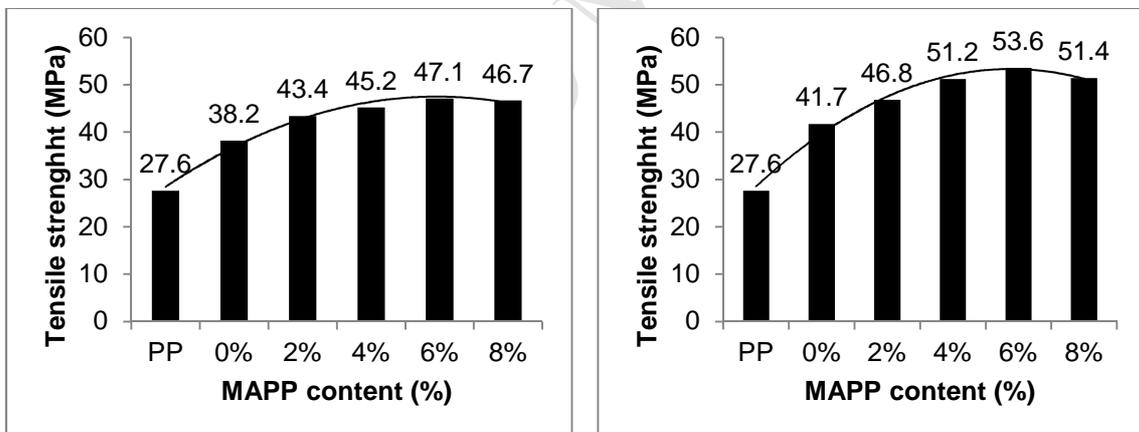
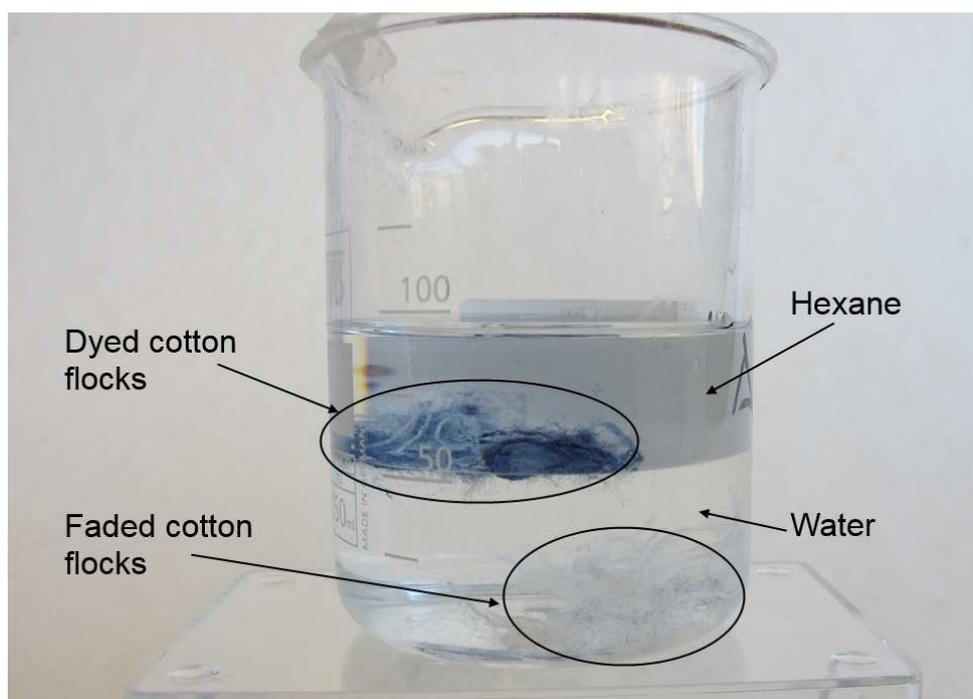


Figure 2: Tensile strength of the composites against its MAPP content. (a) composites with a 30% of cotton strands, (b) composites with a 40% of cotton strands

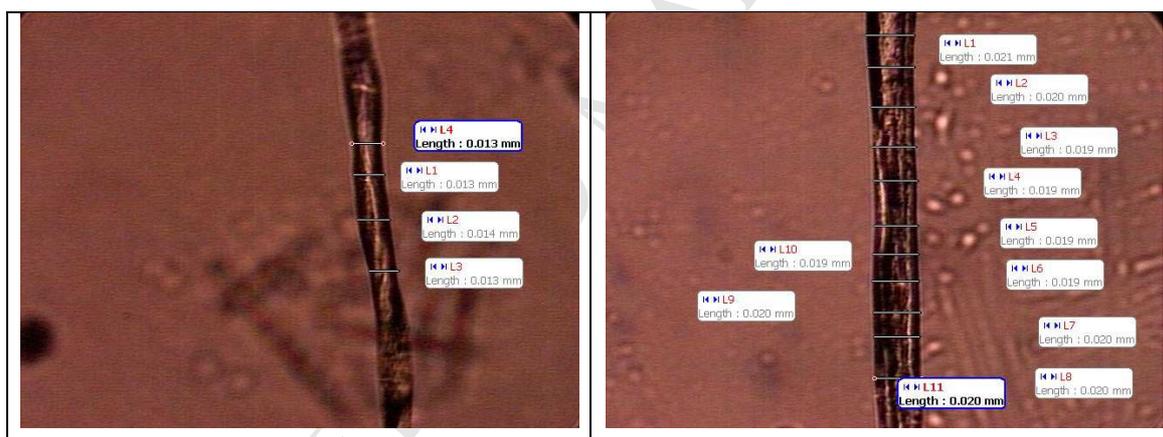


8

9

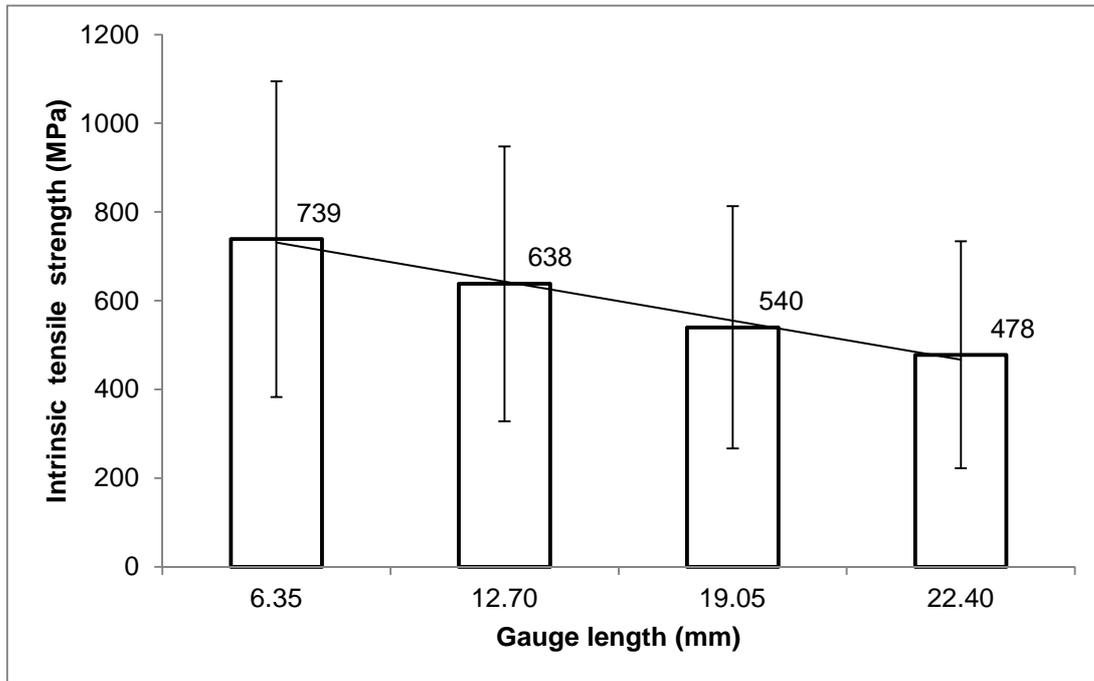
Figure 3: Dyed and faded cotton residue suspended in a water/hexane mixture.

10



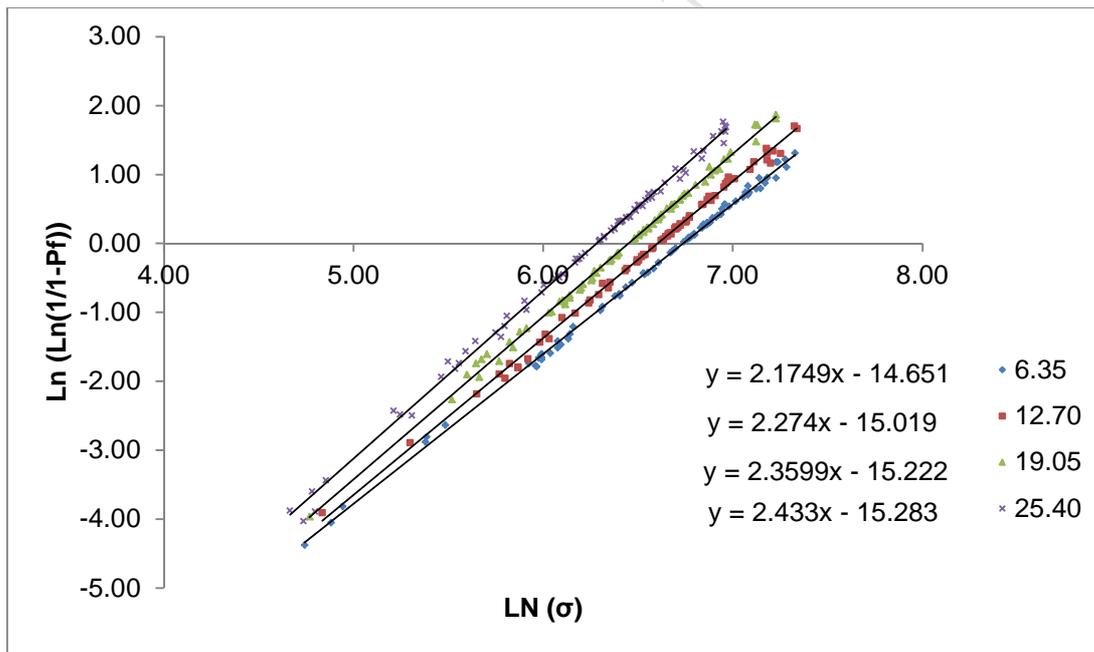
11

Figure 4: Evaluation of the mean diameter of the single cotton fibers.



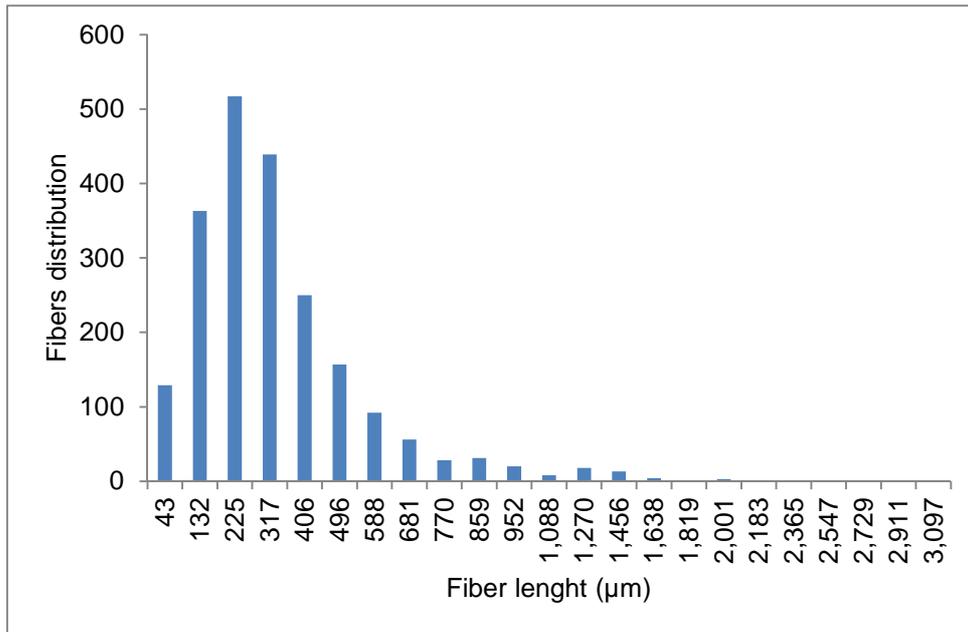
12

13 Figure 5: Intrinsic tensile strength of the dyed cotton strands submitted to single fiber tensile test,
 14 against the gauge length



15

16 Figure 6: Linearized cumulative probability of failure against the natural logarithm of the
 17 measured fiber tensile strengths for each gauge length.



18

19

Figure 7: Fiber length distribution of the WCS extracted from the 40% reinforced coupled composite.

20