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1 Synergistic effect of cellulose nanocrystals/graphene oxide
2 nanosheets as functional hybrid nanofiller for enhancing
3 properties of PVA nanocomposites

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Abstract

Novel functional hybrid nanofillers composed of cellulose nanocrystals (CNC) and graphene oxide nanosheets (GON), at different weight ratios (2:1; 1:1 and 1:2), were successfully prepared and characterized, and their synergistic effect in enhancing the properties of poly (vinyl alcohol) (PVA) nanocomposites was investigated. Due to the synergistic reinforcement, it was found that the Young's modulus, tensile strength and toughness of the PVA nanocomposite containing 5 wt% hybrid nanofiller (1:2) were significantly improved by 320%, 124% and 159%, respectively; and the elongation at break basically remained compared to the neat PVA matrix. In addition, the glass and melting temperatures as well as the moisture sorption of nanocomposites were also enhanced. This synergistic effect improved the dispersion homogeneity by avoiding the agglomeration phenomenon of nanofillers within the polymer matrix, resulting in nanocomposites with largely enhanced properties compared to those prepared from single nanofiller (CNC or GON). The preparation of these hybrid nanofillers and their incorporation into a polymer provided a novel method for the development of novel multifunctional nanocomposites based on the combination of existing nanomaterials.

Keywords

Cellulose nanocrystals; graphene oxide; hybrid nanofiller; nanocomposite; synergistic reinforcement; mechanical properties.

42 1. Introduction

43 In the past two decades, polymer nanocomposite materials have drawn tremendous
44 interest from both scientists and engineers due to their improved properties caused by the
45 inclusion of nanoscale fillers. Novel functional nanocomposites have been constantly
46 emerging in industry applications (Hu, Kulkarni, Choi, & Tsukruk, 2014; Njuguna, Silva, &
47 Sachse, 2011). The polymer nanocomposites consist of a polymeric matrix and a dispersed
48 filler, where at least one dimension is <100 nm (Rodríguez-González et al., 2012). The
49 nanometric scale and the type of nanofiller provide an important effect to the polymer matrix,
50 improving the resulting properties of nanocomposites in comparison with those of an
51 individual component (Chivrac, Pollet, & Avérous, 2009; Paul & Robeson, 2008). It was
52 reported that the reinforcement in polymer nanocomposites depends strongly on the
53 dispersion of nanofillers in the polymer matrix and the interfacial interaction between
54 nanofillers and the polymer matrix (Jose & Thomas, 2014a). Recently, hybrid reinforcements
55 of polymer nanocomposites are gaining increased acceptance. In this context, the combination
56 of two kinds of nanofillers in one functional hybrid nanofiller has attracted great interest
57 (Dhibar, Bhattacharya, Ghosh, Hatui, & Das, 2014; George et al., 2014; Jose & Thomas,
58 2014a; Tang et al., 2009). Indeed, hybrid nanofillers can be designed to achieve a synergistic
59 effect and endow a hot matrix with better performance (Wang et al., 2014a).

60 Recent studies on nanocomposites based on hybrid nanofillers have been focused mainly
61 on thermoplastics and thermosets (Chatterjee et al., 2012; Jose & Thomas, 2014a, b; Wang et
62 al., 2014a; Yuan et al., 2014). In these nanocomposite systems, the synergistic effect of two
63 kinds of nanofillers was the key factor in improving the physico-chemical properties.
64 Depending on the shape, size and surface characteristics of each nanofiller type and the way
65 they are combined, a change in the morphology and microstructure is expected (Jose &
66 Thomas, 2014a, b; Tang, Hackenberg, Fu, Ajayan, & Ardebili, 2012). In most cases, a 3-D

67 interconnected microstructural network can be formed when two kinds of nanofillers are
68 combined in one hybrid nanofiller, which drastically affect the properties of the resulting
69 nanocomposites (Jose & Thomas, 2014a, b). Currently, various hybrid nanofillers have been
70 used as reinforcements for high performance nanocomposites. Table 1 summarizes some
71 hybrid nanofillers that were recently used in nanocomposites development. In most cases, the
72 use of such hybrid nanofillers as a reinforcing phase was achieved in order to enhance the
73 properties of nanocomposites, to introduce some novel properties, or to solve some problems
74 lie to the agglomeration phenomenon and/or interfacial adhesion.

75 In the current investigation, we demonstrate that the combination of 1-D needle like
76 cellulose nanocrystals (CNC) and 2-D flake-like graphene oxide nanosheets (GON) can
77 engender the formation of 3-D hybrid nanofiller, which is suitable for polymer nanocomposite
78 development. The GON (up to 5 μ m in lateral size and about 0.8-1.2 nm in thickness) are
79 essentially graphene nanosheets on which oxygen-containing functional groups are thought to
80 be present in the form of carboxyl, hydroxyl and epoxy groups (El Achaby et al., 2012a, b;
81 Rodríguez-González et al., 2012; Szabo et al., 2006). Currently, GON have been widely used
82 as a single nanofiller for enhancing the properties of water-soluble polymer (El Achaby,
83 2012a; El Achaby et al., 2014; Layek et al., 2013; Rodríguez-González et al., 2012; Xu,
84 Hong, Bai, Li, & Shi, 2009). In this context, it was reported that the incorporation of low
85 GON content (< 3 wt%) into a polymer matrix enhanced the properties of resulting
86 nanocomposite materials. Unfortunately, at high loading level (>3 wt%) the agglomeration
87 tendency can limit its reinforcing efficiency (Jose, Al-Harhi, Al Maadeed, & Dakua, 2015;
88 Xu et al., 2009; Zhang, Zhang, & Madbouly, 2015). Alternatively, the combination of GON
89 with other nanomaterial can bridge adjacent nanosheets and inhibit their aggregation, which
90 enables the material to achieve its highest potential for improving the performance of
91 nanocomposites (Li, Yang, Yu, Zheng, & Liao, 2011; Zhang, Huang, Tjiu, Fan, & Liu, 2012).

92 Due to its large surface area, high modulus, low density, biocompatibility and
93 biodegradability behaviors, CNC have been widely used as nanofillers to enhance the
94 properties of nanocomposites (El Miri et al., 2015a, b). The CNC can have a rod-, ribbon- or
95 needle-like shapes, with a length ranging from 100 nm to 1–2 μm , and a diameter of about 5–
96 20 nm (El Miri et al., 2015a, b). Additionally, CNC with high crystallinity and controlled
97 morphology can be extracted from renewable biosourced materials, such as sugarcane
98 bagasse, the by-product used in this work for CNC extraction (El Miri et al., 2015a).

99 Due to the hydrophilic nature of CNC and GON, their combination can be resulted in the
100 formation of a new hybrid nanofiller. It is worth noting that the abundant oxygen containing
101 groups decorated in GON would interact with the hydroxyl groups and oxygen atoms in CNC,
102 which is beneficial to homogeneously disperse the CNC and the GON in the formed hybrid
103 nanofiller. Relatedly, CNC and GON have recently been combined to form new structures,
104 such as hybrid composite films (Chen et al., 2014; Sadasivuni et al., 2015; Valentini,
105 Cardinali, Fortunati, Torre, & Kenny, 2013).

106 The main objective of this study is to broaden the application of existing
107 nanomaterials (CNC and GON) *via* their combination into a novel hybrid nanofiller for
108 nanocomposites development. This was accomplished by taking into account the so-
109 called synergistic effect of 1-D elongated CNC and 2-D exfoliated GON, which leads
110 in the formation of a network microstructure. This synergistic effect improved the
111 dispersion homogeneity by avoiding the agglomeration phenomenon of nanofiller
112 within the polymer matrix, resulting in nanocomposite materials with largely enhanced
113 properties compared to those prepared from single component nanofiller (like CNC or
114 GON). Herein, the mixing of CNC and GON occurred in water and the obtained hybrid
115 nanofiller (coded as C:G hybrid nanofiller) was characterized and successfully used as a novel
116 functional hybrid nanofiller to produce high performance PVA nanocomposite films *via* the

117 solvent casting method. For this purpose, the weight loading level of C:G hybrid nanofiller
118 was fixed at 5 wt%, and the obtained results were compared with those found by adding 5
119 wt% of either CNC or GON. Additionally, in order to understand the synergistic effect
120 generated from the combination of both kinds of nanomaterials, three C:G hybrid nanofillers
121 have been prepared by varying their weight ratio (i.e C:G-2:1, C:G-1:1 and C:G-1:2). The
122 preparation of these hybrid nanofillers and their incorporation into the polymer matrix provide
123 a promising route for developing innovative materials, mainly by improving the mechanical
124 properties of nanocomposite films in applications where good strength and flexibility are
125 required, such as in food packaging applications.

126 **2. Materials and experimental detail**

127 **2.1 Materials**

128 The sugarcane bagasse (SCB) was provided by a SUNABEL-COSUMAR Group, a
129 company located in the region of Gharb-Loukkos, Morocco. Firstly, the SCB was ground
130 using a precision grinder (Fritsch-Pulverisette 19, GmbH) equipped with a 1 mm sieve. Then,
131 this fraction was sifted in a 150 mm size sieve (Fritsch mesh) to remove small particles. The
132 moisture content of the raw SCB was about 7 wt%. The natural powder graphite ($\leq 20 \mu\text{m}$;
133 99.99%) was purchased from Sigma-Aldrich. The polyvinyl alcohol (molecular weight:
134 10,000–26,000; 86–89% hydrolyzed; CAS: 9002-89-5) was purchased from Alfa-Easer.
135 Analytical grade chemicals used for CNC extraction and GON preparation were purchased
136 from Sigma-Aldrich and used without further purification.

137 **2.2 Preparation of CNC**

138 CNC aqueous suspension was prepared from SCB by using the sulfuric acid hydrolysis
139 process according to our previous works (El Miri et al., 2015a, b). Briefly, the ground SCB
140 fibers were washed with distilled water for 1 hour at 60 °C under mechanical stirring. Then,
141 the prewashed SCB fibers were treated three times with 4 wt% NaOH solution at 80 °C for 2

142 hours under stirring, and bleached with a solution made by equal parts of acetate buffer,
143 aqueous chlorite (1.7 wt% in water) and distilled water. The bleaching treatment was
144 performed 4 times at 80 °C, under mechanical stirring, during 4 hours for each one. Acid
145 hydrolysis was achieved at 55 °C with 64 wt% sulfuric acid for 30 minutes under mechanical
146 stirring. Then, the mixture was diluted with ice cubes to stop the reaction and was washed by
147 successive centrifugations at 12000 rpm at 15 °C for 30 minutes at each step and dialyzed
148 against distilled water until it reached neutral pH. Afterward, the obtained CNC aqueous
149 suspension was homogenized by the use of a probe-type ultrasonic homogenizer (Branson
150 sonifier model 450) for 5 minutes in an ice bath. The concentration of the obtained CNC
151 aqueous suspension was measured at 3.76 mg/mL (Figure 1). Finally, a small quantity of the
152 homogenized CNC suspension was freeze-dried (Christ Alpha 2-4 LD Freeze Dryer) to obtain
153 the CNC in solid form for characterizations.

154 **2.3 Preparation of GON**

155 GON aqueous suspension was prepared *via* chemical oxidation of natural graphite
156 followed by sonication assisted water-phase exfoliation according to our previous works (El
157 Achaby et al., 2012a, b; El Achaby et al., 2013a, b; El Achaby et al., 2014). Firstly, the
158 graphite oxide (oxidized graphite) was prepared according to Hummers methods (Hummers &
159 Offeman, 1958). In this procedure, H₂SO₄, NaNO₃ and KMnO₄ were used to oxidize the
160 graphite after which dilution and washing were performed with distilled water. Residual
161 metallic ions were removed by the use of hydrogen peroxide and hydrochloric acid. The
162 graphite oxide was then isolated through centrifugation and drying. To exfoliate graphite
163 oxide into individual GON, the desired amount of graphite oxide was dispersed in water and
164 then sonicated for 1 hour, resulting in yellow-brownish GON aqueous suspension with a
165 concentration of 1.5 mg/mL (Figure 1). Finally, a small quantity of the obtained GON

166 suspension was freeze-dried (Christ Alpha 2-4 LD Freeze Dryer) to obtain the GON in solid
167 form for characterizations.

168 **2.4 Preparation of C:G hybrid nanofiller**

169 For the preparation of the C:G hybrid nanofiller, the as pre-prepared CNC and GON
170 aqueous suspensions were used after adjusting their concentrations. Three C:G hybrids were
171 prepared by varying the mass ratio of each material (2:1, 1:1 and 1:2) and the three mixtures
172 were prepared as follows: 15 mL of CNC aqueous suspension containing the desired amount
173 of CNC was mixed with 35 mL of GON aqueous suspension containing the desired amount of
174 GON, and the obtained mixtures of CNC and GON were stirred for 15 minutes and sonicated
175 for 2 hours (Ultrasonic System, SharperTek® Stamina XP™, 50 W) at room temperature,
176 resulting in well-homogenized C:G suspensions with a total concentration of 1.5 mg/mL
177 (Figure 1). The samples were coded as C:G-2:1, C:G-1:1 and C:G-1:2 for C:G hybrids at mass
178 ratio of 2:1, 1:1 and 1:2, respectively. It should be noted that C:G hybrids in powdered form
179 were also prepared for characterizations, using the freeze-drying process.

180 **2.5 Preparation of PVA nanocomposite films**

181 Nanocomposite films of PVA-CNC, PVA-GON and PVA-C:G were prepared using the
182 solvent casting method. The loading level of CNC, GON and C:G hybrid nanofillers in
183 nanocomposites was fixed at 5 wt%. For the PVA-C:G nanocomposite films, three different
184 samples were prepared using the three pre-prepared C:G hybrid nanofillers (C:G-2:1, C:G-1:1
185 and C:G-1:2). Three similar PVA solutions were prepared by dissolving 1.425 g (95 wt% in
186 nanocomposites) of PVA in 20 mL of water, under continuous stirring, for 30 minutes at 90
187 °C. The solutions were then cooled to room temperature and allowed to stand in order to
188 remove any air bubbles. Then, each PVA solution was mixed with each pre-prepared C:G
189 suspension (C:G-2:1, C:G-1:1 and C:G-1:2). It must be noted that each C:G suspension
190 contains a total solid mass of 75 mg suspended in 50 mL of water (see above), which

191 corresponds to 5 wt% in regard to the total mass of nanocomposites. Next, each PVA-C:G
 192 mixture was continuously stirred for 2 hours at room temperature to get a homogeneous
 193 mixture of well-dispersed C:G hybrid in PVA solution. Afterward, the final PVA-C:G
 194 mixtures were poured into Petri dishes, and the water evaporated at room temperature for 2
 195 days. Finally, the obtained films were dried for 2 hours at 80 °C for complete removal of
 196 water. The films were coded as PVA-C:G-2:1, PVA-C:G-1:1, and PVA-C:G-1:2. Exactly the
 197 same procedure was applied to prepare films of neat PVA and PVA nanocomposites
 198 containing only CNC or GON; and the films were coded as PVA, PVA-CNC, PVA-GON.

199 **Table 1:** List of some hybrid nanofillers recently used as reinforcement for high
 200 performance polymer nanocomposites.

Hybrid nanofiller	Reference
Graphene/carbon nanotubes (CNT)	(Dhibar et al., 2014; Chatterjee et al., 2012; Zhang et al., 2012; Li et al., 2015; Shen, Pei, Liu, & Fu, 2014; Yi, Yoo, Mahapatra, Kim, & Cho, 2014; Zhang et al., 2013)
Graphene/SiC nanowires	(Wang et al., 2014a)
Graphene/nanoclay	(Wang et al., 2014b)
Graphene/Fe ₃ O ₄ nanoparticles	(Zhang et al., 2014)
Graphene/boehmite	(Yuan et al., 2014)
layered double hydroxide /CNT	(Huang et al., 2010)
CNT/ fullerene-like tungsten disulfide	(Naffakh, Diez-Pascual, Marco, & Ellis, 2012)
CNT/nanoclay	(Tang et al., 2009; Tang et al., 2012; Pradhan, Roy, Srivastava, & Saxena, 2015)
Nanoclay/Al ₂ O ₃ nanoparticles	(Jose & Thomas, 2014a, b)
CNC/Ag nanoparticles	(George et al., 2012; George et al., 2014; Yu et al., 2014; Xu, Yang, Xing, Yang, & Wang, 2013; Fortunati et al., 2013a)

201

202 **2.6 Characterization techniques**

203 The zeta potential measurements were carried out using a Malvern Zetasizer Nano ZS
 204 instrument. Measurements were made at 23 °C using 1 mL of diluted suspensions (0.25
 205 mg/mL) of CNC, GON and C:G samples. Immediately before being analyzed, diluted
 206 suspensions were sonicated for 5 minutes in an ultrasonic bath (Ultrasonic System,
 207 SharperTekVR Stamina XPTM, 50 W) and then transferred to a folded capillary cell (DTS

208 1060, Malvern Instruments). Atomic Force Microscopy (AFM) measurements were carried
209 out using a Veeco Dimension ICON. Tapping mode was used to capture height images at a
210 scan rate of 1.5 Hz. Samples for AFM observations were prepared by depositing a droplet of
211 diluted suspensions onto freshly cleaved mica sheets, and allowing the solvent to dry in air.
212 The morphology observation was performed using a Scanning Electron Microscope (SEM)
213 (FEI, Quanta 200-ESEM) operating at an accelerating voltage of 20 kV. Immediately before
214 being analyzed, samples were coated by a thin conductive carbon layer to help improve SEM
215 observations. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed
216 on an ABB Bomem FTLA 2000 spectrometer equipped with a Golden Gate single attenuated
217 total reflection (ATR) cell. The experiments were carried out in the range of 4000–400 cm^{-1}
218 with a 4 cm^{-1} resolution and an accumulation of 32 scans. The FTIR spectra were taken in the
219 transmittance mode. Thermogravimetric Analyses (TGA) were carried out under nitrogen
220 atmosphere at a heating rate of 10 $^{\circ}\text{C}.\text{min}^{-1}$ from 25 to 700 $^{\circ}\text{C}$, using a TGA-Q500 (TA
221 Instrument). Differential Scanning Calorimetry (DSC) was carried out under nitrogen gas
222 with a 10 $^{\circ}\text{C}.\text{min}^{-1}$ heating rate from -50 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$, using a DSC-Q100 (TA Instrument).
223 Tensile tests were performed using an Instron 8821S tensiometer. The tensile specimens were
224 cut in rectangular shapes with dimensions of 80 mm in length and 10 mm in width. The gauge
225 length was fixed at 30 mm and the speed of the moving clamp was 5 mm/min. All tests were
226 carried out on a minimum of five samples and the reported results are average values.
227 Moisture uptake measurements were carried out according to the method used by
228 Soykeabkaew et al. (2012). Briefly, strips with specific dimensions (10 mm \times 40 mm) were
229 dried at 105 $^{\circ}\text{C}$ for 2 hours in an oven. After being weighted, the dried films were inserted in
230 a climatic chamber containing a saturated NaCl solution with controlled relative humidity
231 (RH) of $75 \pm 0.5\%$ at 25 $^{\circ}\text{C}$. Thereafter, the samples were removed at specific intervals (each

232 hour) over the duration of 6 hours and weighted using a digital balance. The moisture uptake
233 of the samples was calculated as follows:

$$234 \text{ Moisture uptake (\%)} = \frac{M_t - M_0}{M_0} \times 100.$$

235 Where M_t and M_0 are the weights of the sample after t_{min} exposure to 75 % RH and of the
236 dried sample before being inserted in the climatic chamber, respectively.

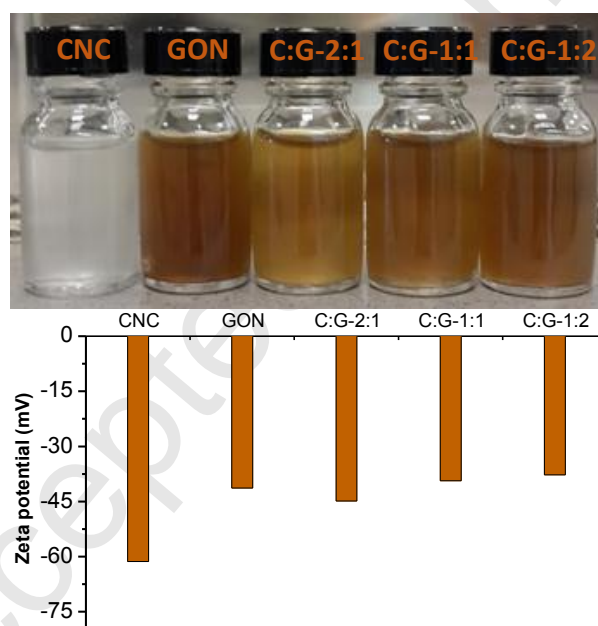
237 3. Results and discussions

238 3.1 Characterization of nanofillers

239 In the present work, pre-prepared CNC and GON aqueous suspensions were used as
240 starting materials to produce three C:G hybrid nanofillers at different mass ratios (2:1, 1:1 and
241 1:2). Figure 1 shows photographs of aqueous suspensions of CNC, GON, C:G-2:1, C:G-1:1
242 and C:G-1:2 obtained by sonication process. These photographs were taken 15 days after their
243 preparation. The measured zeta potential of these suspensions is also illustrated in Figure 1.
244 As seen in this Figure, the CNC aqueous suspension showed a good stability, in which a white
245 gel appearance was observed. It is well known that, after their homogenization, CNC are
246 stable in water because of their surface functionalities and the ability of the water solvent and
247 surface groups to counterbalance the attractive hydrogen-bond interactions exerted by the
248 abundant hydroxyl groups on the surface of CNC (El Miri et al., 2015a, b). Additionally, the
249 zeta potential of the as-prepared CNC suspension showed a value of -61.3 mV (Figure 1).
250 Consequently, the CNC suspension was considered stable because the absolute value was
251 higher than 25 mV (El Miri et al., 2015a, b). On the other hand, suspended individual
252 nanosheets of GON were obtained by intense sonication in water of completely oxidized
253 natural graphite (graphite oxide) (El Achaby et al., 2012a, b; El Achaby et al., 2013a, b; El
254 Achaby et al., 2014). Remarkably, it should be noted that the GON suspension exhibited
255 strong and long-term stability in water (Figure 1). This was due to the hydrophilic oxygen
256 groups attached to the GON's basal plane and edges (Rodríguez-González et al., 2012; Szabo

257 et al., 2006). The zeta potential of GON suspension was measured at -41.3 mV, which is
 258 comparable to previous works (Chen et al., 2014; Li, Muller, Gilje, Kaner, & Wallace, 2008).

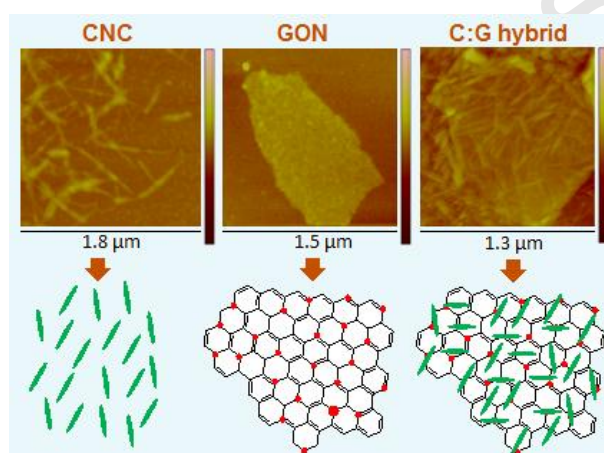
259 By mixing both CNC and GON aqueous suspensions, at different mass ratios, *via*
 260 stirring and sonication process, stable mixtures were obtained (Figure 1). This was
 261 unsurprisingly because the hydrophilic nature of both kinds of nanomaterials and their good
 262 interfacial compatibility. The values of the measured zeta potential of these mixtures were
 263 found to be -44.8 , -39.3 and -37.7 mV for C:G-2:1, C:G-1:1 and C:G-1:2 samples,
 264 respectively. Remarkably, the zeta potential of CNC suspension (-61.3 mV) was reduced
 265 after its mixture with GON suspension, confirming that interfacial interactions throughout
 266 hydrogen bonding occurred in the C:G hybrid mixtures.



267
 268 **Figure 1:** Photographs of aqueous suspensions and zeta potential values of CNC, GON
 269 and C:G hybrids (C:G-2:1, C:G-1:1 and C:G-1:2).

270 AFM observations were used to investigate the morphology and dimensions of CNC
 271 and GON nanomaterials and their C:G hybrid nanofillers. Examples of the obtained AFM
 272 images are illustrated in Figure 2. For CNC, the AFM image showed that the as-extracted
 273 CNC had needle-like nanoparticles, confirming that their extraction from the treated SCB was

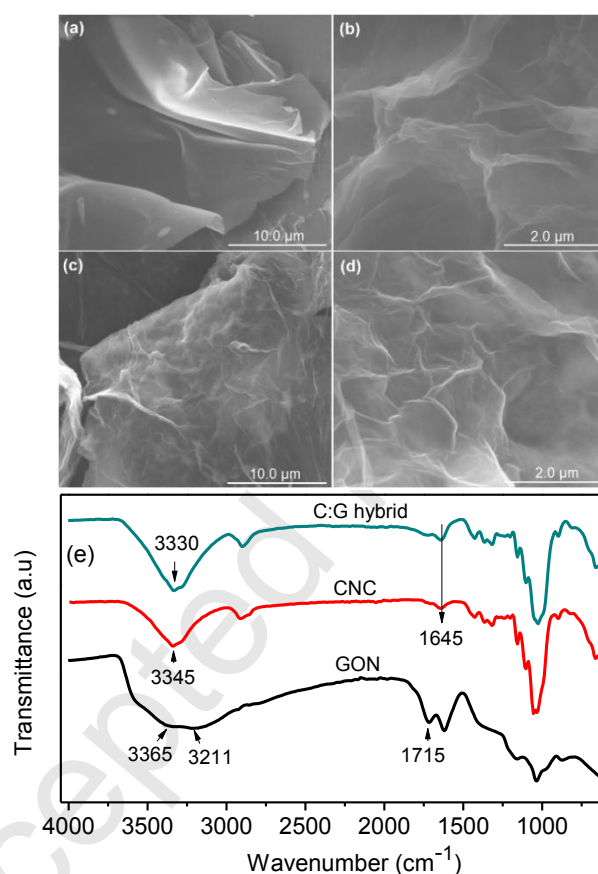
274 successful. Furthermore, the average diameter and length of the as-extracted CNC were found
 275 to be 5 ± 1.1 nm and 275 ± 73 nm, respectively. These results coincide with those reported by
 276 Teixeira et al. (2011), especially in relation to the geometry and dimensions of CNC obtained
 277 from SCB by 6 M sulfuric acid hydrolysis. On the other hand, the AFM images of the GON
 278 revealed the presence of irregular shaped individual nanosheets with uniform thickness and
 279 different lateral dimensions (El Achaby et al., 2014), an example of an individual nanosheet is
 280 shown in Figure 2. The lateral dimensions of nanosheets range from ~ 100 nm to ~ 2 μ m while
 281 the thickness was measured at ~ 0.9 nm (El Achaby et al., 2012a; El Achaby et al., 2014).



282
 283 **Figure 2:** Tapping mode AFM images and schematic illustrations of CNC, GON and C:G
 284 hybrid (C:G-1:2) (the red dots are the oxygen containing groups in GON).

285 For the AFM image of C:G hybrid nanofiller (C:G-1:2), one can see that the surface of
 286 GON has become totally and densely covered with randomly arranged CNC (Figures 2). The
 287 exact dimensions of C:G hybrid nanofillers cannot be measured accurately. The size of these
 288 nanofillers was controlled by the initial size of CNC and GON, and the thickness cannot be
 289 measured because the CNC were attached to the surfaces and edges of GON, forming a 3-D
 290 interconnected network microstructure, as schematically illustrated in the bottom of Figure 2.
 291 Previous works investigating the graphene-based hybrid nanofillers demonstrated that, in all
 292 cases, the graphene nanosheets were decorated after their combination with other
 293 nanomaterials such as aramid nanofibers (Fan, Shi, Zhang, Wang, & Yin, 2012), Fe_3O_4

294 nanoparticles (Zhang et al., 2014), CNT (Chatterjee et al., 2012; Zhang et al., 2012), SiC-
 295 nanowires (Wang et al., 2014a), and boehmite (Yuan et al., 2014), forming a new
 296 interconnected microstructure. This behavior was ascribed to the 2-D flat surface of graphene,
 297 which is exposed to absorb other compatible nanosized materials. Herein the CNC and GON
 298 are compatible nanomaterials because they have similar surface functionalities, especially the
 299 oxygen containing groups, resulting in the formation of such hybrid nanofiller.

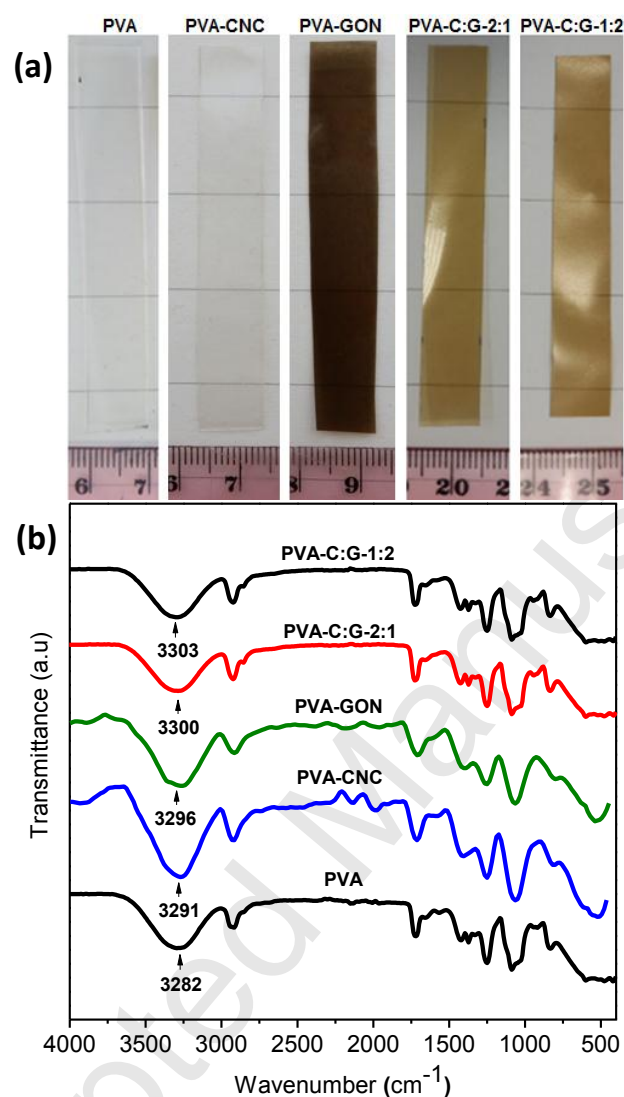


300
 301 **Figure 3:** MEB images of (a,b) GON and (c,d) C:G hybrid (C:G-1:1) and (e) FTIR
 302 spectra of CNC, GON and C:G hybrid (C:G-1:1).

303 Figures 3a-d present SEM images of the freeze dried GON and the C:G hybrid (C:G-
 304 1:1). It is clearly evident that the exfoliated GON exist as flakes (agglomerated sheets) with a
 305 smooth surface and distinct bent edges (Figure 3a,b). However, in the C:G hybrid nanofiller,
 306 CNC appear to be homogeneously dispersed among GON flakes (Figures 3c,d). Additionally,
 307 the SEM image of C:G hybrid at low magnification shows the formation of an interconnected

308 network between GON and CNC, leading to a 3-D like network microstructure (Figure 3d).
309 This morphology was also observed in other hybrids prepared by the combination of 1-D and
310 2-D nanomaterials, such as CNT/clay platelets (Pradhan et al., 2015), LDH/CNT (Zhao,
311 Zhang, Huang, & Wei, 2012), and graphene/CNT (Tang et al., 2012).

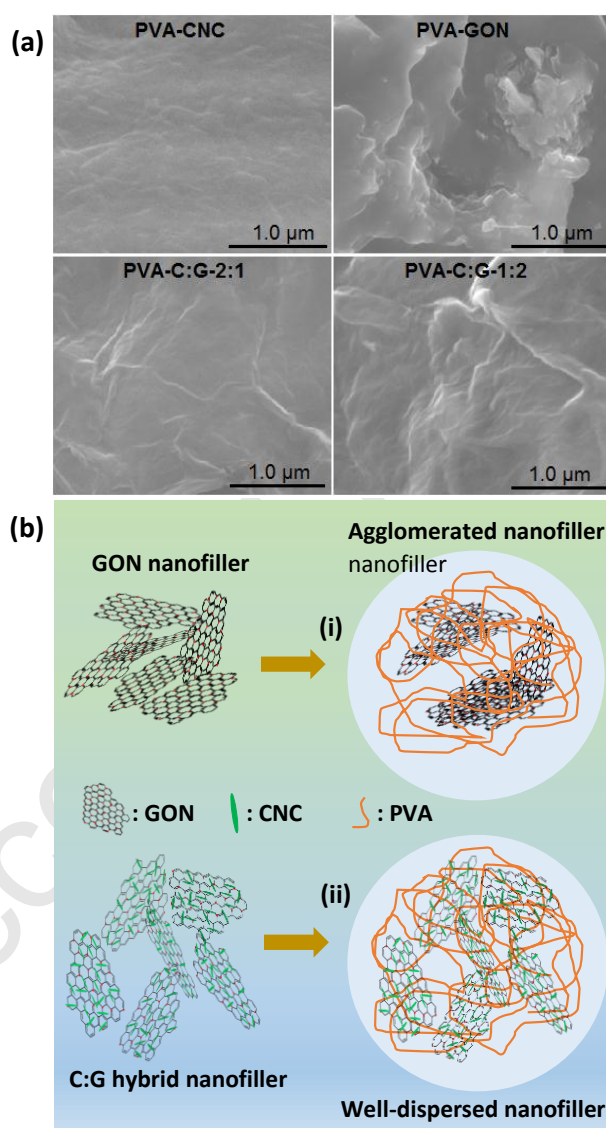
312 Figure 3e shows FTIR spectra of CNC, GON and C:G hybrid (C:G-1:1). In the FTIR
313 spectrum of CNC, the peaks found at 2914 and 1369 cm^{-1} are assigned to C-H stretching and
314 bending vibrations. The peaks observed at 1429 and 1055 cm^{-1} are assigned to the vibrations
315 of O-H and C-O, respectively. The broad band centered at 3345 cm^{-1} is associated with O-H
316 bonds in hydroxyl groups. The peak at 1645 cm^{-1} is associated with intramolecular hydrogen
317 bonds (El Miri et al., 2015a; Valentini et al., 2013). For the GON spectrum, the bands at 3365
318 and 3211 cm^{-1} are associated to the stretching of O-H bonds in hydroxyl groups. The band at
319 1715 cm^{-1} is attributed to the C=O carbonyl stretching, and the bands at 1038 and 973 cm^{-1}
320 are associated to the epoxide groups C>O vibration (El Achaby et al., 2012a; El Achaby et al.,
321 2014). Looking at the C:G hybrid nanofiller, the bands at 3345 cm^{-1} , 3365 and 3211 cm^{-1} that
322 are associated to the hydroxyl groups in CNC and GON spectra, respectively, were shifted to
323 a new band at 3330 cm^{-1} in the spectrum of the C:G hybrid nanofiller. Additionally, the band
324 at 1715 cm^{-1} that is associated to the carbonyl groups observed in GON spectrum was
325 overlapped with that observed at 1645 cm^{-1} in C:G spectrum, which is associated to the
326 intramolecular hydrogen bonds in CNC. These results confirm that strong hydrogen
327 interactions occur in the C:G hybrid nanofillers (Valentini et al., 2013). Recently, successful
328 combinations of CNC and GON in the form of hybrid composite films have been reported in
329 the literature, by taking into account the hydrogen interaction and the interfacial compatibility
330 between CNC and GON surfaces (Chen et al., 2014; Sadasivuni et al., 2015; Valentini et al.,
331 2013). Herein, the combination of CNC and GON in a hybrid nanofiller should act as a
332 stronger reinforcing agent for polymers causing synergistic effects.

333 **3.2 Processing and structural characterization of PVA nanocomposites**

334
335 **Figure 4:** (a) Digital images and (b) FTIR spectra of neat PVA and its
336 nanocomposite films with CNC, GON and C:G hybrid (C:G-2:1 and C:G-1:2).

337 The mixing of the PVA polymer with CNC, GON and C:G hybrid nanofillers in water
338 was easily achieved in controlled conditions, enabling the formation of a homogeneous and
339 stable aqueous mixtures. By casting all mixtures on plastic dishes and evaporating of the
340 water, films with high quality and good flexibility were produced. Figure 4a shows digital
341 images of the produced films of unloaded PVA, PVA-CNC, PVA-GON and PVA-C:G (PVA-
342 C:G-2:1 and PVA-C:G-1:2). As shown in these images, the visual transparency of PVA was
343 not affected by the addition of CNC and a clear dark color was observed for PVA-GON

344 nanocomposite film. In consequence, an intermediate color was observed for PVA-C:G films.
 345 This behavior is mainly associated with the initial color of each nanofiller suspension (Figure
 346 1). This result indicated that the components of each formulation were well mixed in the
 347 chosen conditions of the preparation. We noted that the thickness of these films was
 348 adjustable by controlling the amount of the solution used for the casting technique (El Miri et
 349 al., 2015a, b).



350
 351 **Figure 5:** (a) SEM micrographs of PVA nanocomposites with CNC, GON and C:G
 352 hybrid (C:G-2:1 and C:G-1:2) and (b) schematic representations of the dispersion state of (i)
 353 GON and (ii) C:G hybrid nanofillers within the PVA polymer matrix.

354 FTIR spectra of PVA and its nanocomposite are shown in Figure 4b. It is well known that
355 the –OH band is sensitive to hydrogen bonding and can be compelled to a shifted
356 wavenumber in FTIR spectra. As shown in Figure 4b, the addition of the C:G hybrid
357 nanofiller within the PVA matrix resulted in shifting the hydroxyl band in the range of 3500–
358 3000 cm^{-1} , indicating the existence of hydrogen bonding interactions between the oxygen
359 containing functional groups on the surface of C:G hybrid nanofiller and the hydroxyl groups
360 on the PVA macromolecular chains. This trend was also observed in CNC- or GON-filled
361 PVA nanocomposite films (Figures 4b), in which hydrogen bonding interactions can occur
362 between the oxygen functional groups of each nanofiller with PVA chains. Similar trends
363 have been reported for CNC-filled PVA (Fortunati et al., 2013b; Peresin, Habibi, Zoppe,
364 Pawlak, & Rojas, 2010), GON-filled PVA (Huang et al., 2012), and Ag-decorated CNC
365 hybrid nanofiller filled PVA (Fortunati et al., 2013a) nanocomposite films.

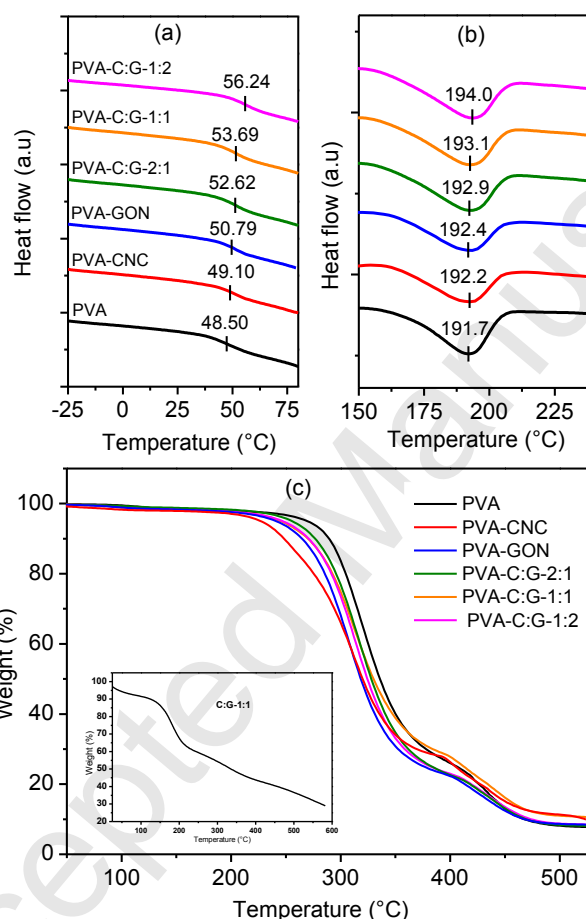
366 Figure 5a shows SEM images of the cryofractured surface of PVA-CNC, PVA-GON,
367 PVA-C:G-2:1 and PVA-C:G-1:2 nanocomposite films. From these images, the PVA-CNC
368 nanocomposite show a homogenous structure in which the CNC are well dispersed with small
369 aggregates, while the GON showed large aggregates in PVA-GON nanocomposite. The
370 aggregation tendency of GON was mainly due to the existence of strong hydrogen bonding
371 between the surface hydroxyl groups of GON, and consequently the sheet–sheet interaction
372 becomes dominant over the sheet–matrix interaction. This type of aggregation may lead to the
373 formation of thicker flakes instead of nanosheets within the polymer matrix, as schematically
374 proposed in the Figure 5b(i) for PVA-GON nanocomposite system. For PVA-C:G
375 nanocomposites, the SEM micrographs clearly indicate that the C:G nanofillers are well-
376 dispersed within PVA matrix (the well-dispersed white lines are the GON and CNC) (Figure
377 5a). No visible nanofiller agglomerates were observed in the nanocomposites. It is believed
378 that the CNC adsorbed on the GON surface could inhibit the sheet-to-sheet aggregations of

379 GON and that the hybrid nanofiller-polymer matrix interfacial adhesion could also be
380 improved. In these nanocomposite films, a 3D interconnected network is assumed to be
381 formed. The special morphology of C:G hybrid nanofiller and its functionalized surface
382 ensure a good homogeneous dispersion within the PVA matrix, as proposed in the scheme of
383 Figure 5b(ii) for PVA-C:G nanocomposite. This was mainly the result of strong interactions
384 between the macromolecular chains of the PVA and the C:G hybrid nanofiller *via* hydrogen
385 bonding. Consequently, the excellent dispersion of C:G hybrid nanofillers within the polymer
386 matrix was directly correlated with its effectiveness in improving the properties of
387 nanocomposite films.

388 **3.3 Thermal properties of PVA nanocomposite films**

389 The effect of nanofillers on glass transition (T_g) and melting (T_m) temperatures of PVA is
390 shown in Figures 6a,b, which were determined from DSC analysis. From the obtained results,
391 it is clear that these thermal parameters were influenced by the addition of 5 wt% CNC (PVA-
392 CNC), 5 wt% GON (PVA-GON) and 5 wt% C:G hybrid nanofillers at various mass ratios
393 (PVA-C:G-2:1, PVA-C:G-1:1 and PVA-C:G-1:2). The T_g illustrated in Figure 6a increases
394 from 48.50 °C for neat PVA to 52.62, 53.69 and 56.24 °C for PVA-C:G-2:1, PVA-C:G-1:1
395 and PVA-C:G-1:2 nanocomposite films, respectively. Additionally, the increase of T_g is
396 accompanied by an increase of T_m from 191.70 °C for neat PVA to 192.93, 193.19 and 194.07
397 °C for PVA-C:G-2:1, PVA-C:G-1:1 and PVA-C:G-1:2, respectively (Figure 6b). These
398 observed values for T_g and T_m were superior to those observed for PVA-CNC (49.10 °C and
399 192.2 °C) and PVA-GON (50.79 °C and 192.4 °C). Consequently, the increase in T_g and T_m
400 suggests that the mobility of PVA macromolecular chains was inhibited, which results from
401 the formation of a cross-linking network between the PVA and C:G hybrid nanofiller through
402 hydrogen bonds between the oxygen-containing functional groups of nanofiller and the
403 hydroxyl groups of PVA chains (Huang et al., 2012). This effect was more pronounced in

404 nanocomposites containing C:G hybrid nanofiller in comparison to those containing only
 405 CNC or GON, and can be ascribed to the synergistic effect generated from the hybrid
 406 nanofiller. This effect is more important for the hybrid nanofiller containing the high amount
 407 of GON (C:G-1:2), because the PVA-C:G-1:2 exhibited the higher T_g and T_m in comparison to
 408 PVA-C:G-1:1 and PVA-C:G-2:1.



409
 410 **Figure 6:** (a) Glass transition temperature and (b) melting temperature obtained from
 411 DSC curves and (c) TGA curves of PVA and its nanocomposites films with CNC, GON and
 412 C:G (C:G-2:1, C:G-1:1 and C:G-1:2) hybrid nanofillers. The TGA curve of the C:G-1:1
 413 hybrid is shown in the inset of (c).

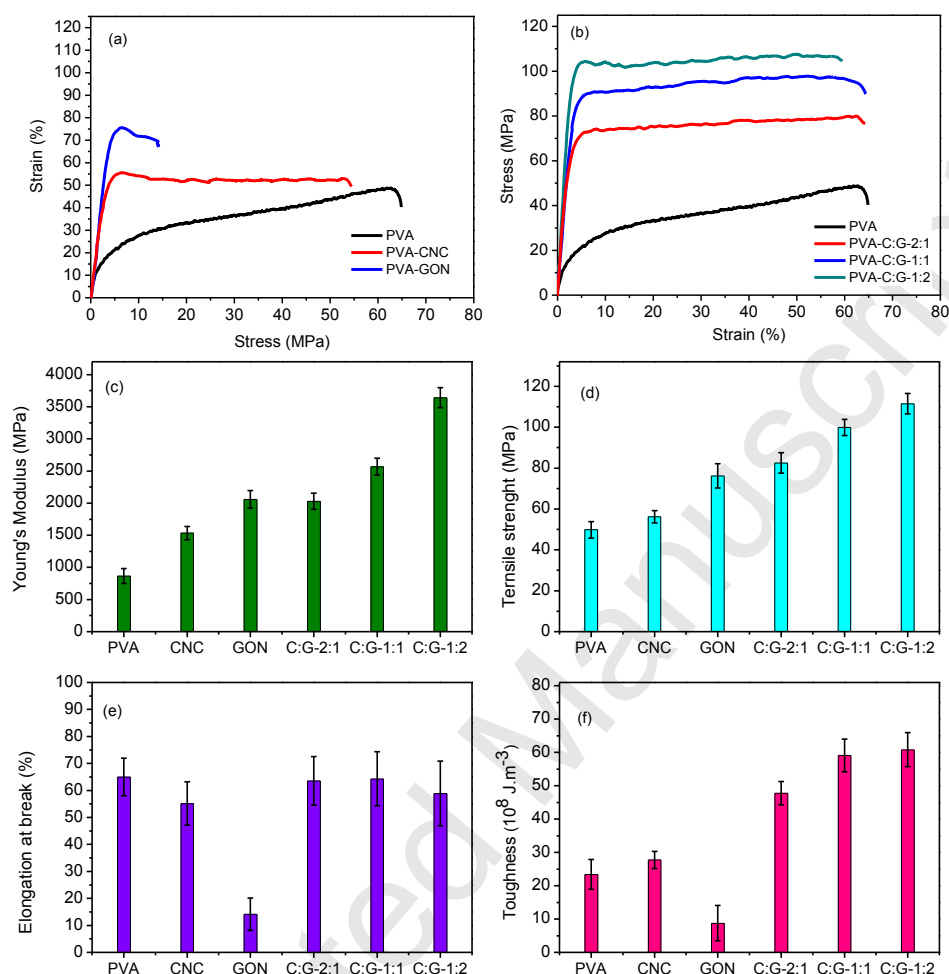
414 Figure 6c shows the TGA curves of neat PVA and its nanocomposites. It is clear
 415 that the onset temperatures (T_{onset}) of nanocomposites are almost identical and slightly
 416 lower than that observed for neat PVA ($T_{onset} = 269$ °C). Herein, the T_{onset} is reported as
 417 the temperature corresponding to 5 % weight loss ($T_{onset} = T_{5\%}$). However, the T_{onset} of

418 nanocomposites containing C:G-2:1, C:G-1:1 and C:G-1:2 was observed at 256, 244
419 and 246 °C, respectively. This behavior was due to the thermal instability of dispersed
420 C:G hybrid nanofillers; an example for C:G-1:1 is shown in the inset of Figure 6c.
421 Importantly, the weight loss observed for C:G hybrid nanofiller around 250 °C (\approx 45
422 %) is absent in the nanocomposite samples, suggesting a good interaction between the
423 oxygen functional groups of the C:G nanofillers and the macromolecular chains of
424 PVA polymer. Comparatively, in nanocomposite films containing only CNC or GON,
425 the T_{onset} was lower than that of all nanocomposites containing C:G hybrid nanofillers
426 (226 °C for CNC and 240 °C for GON), which was ascribed to the fine dispersion of
427 the C:G hybrid nanofillers within the PVA polymer, thus confirming that the
428 synergistic effect between CNC and GON existed in PVA-C:G nanocomposites.

429 ***3.4 Mechanical properties of PVA nanocomposite films***

430 The mechanical properties of PVA and its nanocomposite films with different
431 nanofillers were investigated by uni-axial tensile testing. Typical stress-strain curves of all
432 films are presented in Figures 7a,b and the measured mechanical parameters are illustrated in
433 Figures 7c-f. From these data, it can be seen that all nanocomposites containing C:G hybrid
434 nanofillers (C:G-2:1, C:G-1:1 and C:G-1:2) exhibited superior mechanical properties than
435 those observed for nanocomposites containing CNC or GON nanofillers, thus confirming that
436 a unique synergistic effect of the C:G hybrid nanofillers on the reinforcing of the PVA was
437 clearly observed. For example, the PVA-C:G-1:2 nanocomposite film exhibited a Young's
438 modulus of 3639.48 MPa and an ultimate tensile strength of 111.45 MPa, which correspond
439 to 320 % and 124 % increases, respectively, in regard to neat PVA. In contrast, the Young's
440 modulus and tensile strength of the PVA-CNC nanocomposite are increased only by 77 and
441 12 %, respectively, as compared to neat PVA, and they are increased by 137 and 53 % in the
442 case of PVA-GON nanocomposite. These results for CNC- or GON-based nanocomposite

443 films were comparable with those already reported in the literature (Fortunati et al., 2013b;
 444 Xu et al., 2009; Xu et al., 2013; Zhang et al., 2014).



445
 446 **Figure 7:** (a,b) Typical stress-strain curves of PVA and its nanocomposites with CNC,
 447 GON and C:G (C:G-2:1, C:G-1:1 and C:G-1:2) hybrid nanofillers, and plot of (c) Young's
 448 modulus, (d) tensile strength, (e) elongation at break and (f) toughness (T) as function of
 449 nanofillers.

450 Consequently, compared with CNC or GON, the C:G hybrid nanofiller showed better
 451 performance in reinforcement of PVA nanocomposite, at the same loading level (5 wt%). This
 452 is because of the synergistic effect induced by the combination of CNC and GON. Such
 453 synergistic interactions resulted in the formation of an interconnected network structure,
 454 which explains the very large increase in tensile properties of the PVA matrix. In the GON
 455 reinforced nanocomposite, the relatively lower mechanical properties were due to the

456 agglomeration phenomenon of nanosheets (Figure 5b(i)) (Jose et al., 2015; Xu et al., 2009;
457 Zhang et al., 2015). These agglomerates may prevent an efficient transfer of load to the
458 nanosheet and may cause a decrease in the aspect ratio. As discussed above, in the C:G hybrid
459 nanofiller, the surface of GON had become decorated with CNC, which could have inhibited
460 the sheet-to-sheet aggregations of GON (Figure 5b(ii)). Also, the interfacial adhesion between
461 the C:G hybrid nanofiller and the polymer matrix could be improved. In consequence, the
462 C:G hybrid nanofiller network acts as an efficient reinforcement in the parent system, which
463 provides superior tensile properties to the nanocomposites. In this case, effective stress
464 transfer occurred from the polymer chains to the dispersed hybrid nanofiller, which provided
465 additional strength to the nanocomposites (George et al., 2014). Similar trends were observed
466 by Zhang et al. (2012) in GON/CNT hybrid nanofiller reinforced PVA nanocomposites,
467 which were attributed to the synergistic effect phenomenon that was generated from the
468 combination of GON and CNT.

469 Interestingly, the elongation at break of the PVA was not largely affected by the
470 addition of different C:G hybrid nanofillers (C:G-2:1, C:G-1:1 and C:G-1:2). These results
471 indicated that the as-developed PVA-C:G nanocomposite films are ductile materials, as the
472 toughness of PVA-C:G nanocomposites was largely improved in comparison with the neat
473 PVA (Figure 7f. This is unusual, as GON-filled nanocomposites become brittle materials with
474 a reduced elongation at break (Figure 7e). Recently, it was demonstrated that the polymer
475 matrix cannot lose its ductility when a hybrid nanofiller is added (George et al., 2014;
476 Pradhan et al., 2015; Wang, Tian, & Zhang, 2010; Xu et al., 2013). The research group of
477 George et al. (2014) demonstrated that the presence of Ag nanoparticles on the surface of
478 CNC helps the polymer to keep its ductility, because the Ag nanoparticles can act as a
479 physical crosslink between the CNC and polymer chains, thus helping polymer chains to
480 move and can keep its elongation properties, with improvement of the other mechanical

481 properties. Herein, PVA chains can form hydrogen bonds with CNC rather than with GON,
482 because the surface of GON is totally and densely covered with CNC, as shown by AFM and
483 SEM observations (Figures 2 and 3). Consequently, in the C:G hybrid nanofillers, the CNC
484 may play the role of cross-linking agents, helping the PVA chains to keep its mechanical
485 ductility. This is possible because the elongation at break of PVA-CNC was measured at
486 55.17 %, which is comparable to that measured for neat PVA (64.98 %) and its
487 nanocomposites containing C:G hybrid nanofillers (58,9-64.29 %), while the elongation at
488 break for PVA-GON was measured at 14.17 %. It is suggested that films suitable for food
489 packaging should preferably strong and flexible. This trend is observed in PVA
490 nanocomposite films reinforced with C:G hybrids fabricated in the present work.

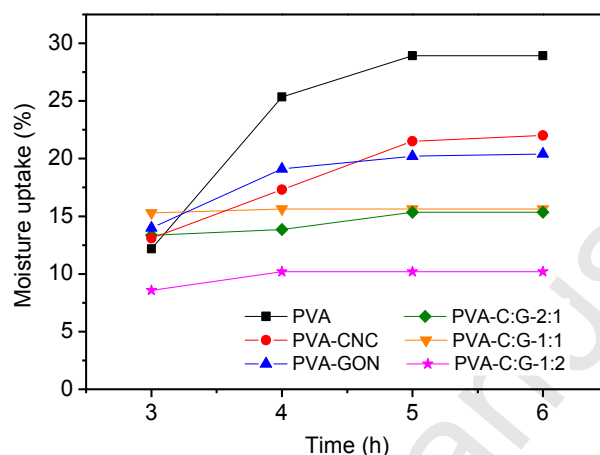
491 From Figure 7, the studied tensile properties were affected by the variation of mass ratio
492 of CNC and GON in the C:G hybrid nanofillers. Notably, the reinforcing efficiency of C:G-
493 1:2 is higher than that of C:G-1:1 and C:G-2:1, because the PVA-C:G-1:2 nanocomposite
494 shows the superior improvement of the tensile properties, while the relatively inferior
495 improvement is observed for the PVA-C:G-2:1 nanocomposite, thus confirming that the
496 synergetic effect was more pronounced in the hybrid nanofiller containing a high amount of
497 GON (C:G-1:2). This can be attributed to the flat surface of the GON which led to an
498 enhanced mechanical interlocking with the polymer chains and an enlarged interphase zone at
499 nanofiller-polymer interface (El Achaby & Qaiss, 2013). This effect was less pronounced in
500 the C:G hybrid nanofiller containing a low amount of GON (C:G-2:1) because the presence of
501 a high amount of CNC can completely cover the surface of GON, and the interphase zone at
502 nanofiller-polymer interface can be reduced. This is possible because the C:G hybrid
503 nanofiller containing equal amounts of CNC and GON shows an intermediate reinforcing
504 efficiency.

505

506 *3.5 Moisture uptake of PVA nanocomposite films*

507 Moisture uptake rate (MUR) was analyzed in order to evaluate the effect of C:G hybrid
508 nanofillers on PVA films at a constant relative humidity (RH). The MUR is a highly
509 important property to consider in certain industries like food packaging. In this application,
510 films should prevent or at least reduce MUR for food preservation. In general, a reduced
511 MUR is required for moisture-sensitive food products (Bilbao-Sainz, Avena-Bustillos, Wood,
512 Williams, & McHugh, 2010; George & Siddaramaiah, 2012). Figure 8 plots the MUR for all
513 studied films as a function of storage time (3-6 hours) upon conditioning at 75 % RH. For all
514 films, it is apparent that the MUR remained constant after a storage time of 5 hours of
515 conditioning, which is known as the equilibrium moisture content (EMC) at a particular RH
516 (George et al., 2014). The neat PVA film had a much greater EMC than its nanocomposites
517 with different nanofillers. The EMC of the neat PVA was observed at 28.93 %, which can be
518 attributed to the hydrophilic nature of the PVA polymer (George et al., 2012). Unlike the neat
519 PVA, the PVA-CNC and PVA-GON nanocomposites exhibited an EMC of 21.84 % and
520 20.30 %, respectively, which is lower than that observed for the neat PVA and higher than
521 that observed for the PVA-C:G nanocomposites. From Figure 8, the nanocomposites of PVA-
522 C:G-2:1, PVA-C:G-1:1 and PVA-C:G-1:2 showed an EMC of 15.36, 15.63 and 10.19 %,
523 respectively. Therefore, it can be concluded that the moisture resistance of the PVA polymer
524 largely improved with the addition of C:G hybrid nanofillers, especially for C:G-1:2 hybrid
525 nanofiller. This improvement can be attributed to the presence of strong hydrogen bonding
526 interactions between the PVA matrix and C:G hybrid nanofillers, which minimizes the
527 interaction of water with the nanocomposites (George et al., 2012, 2014). This trend was also
528 reported by George et al. (2014) who demonstrated that the hydrogen bonding interactions
529 could reduce the number of sorption sites available for moisture absorption in the hydrophilic
530 polymer based nanocomposites, reducing the EMC at a high RH. Herein, the well-dispersed

531 C:G hybrid nanofiller acted as an interpenetrated network within the PVA matrix and
 532 prevented moisture absorption in the nanocomposite films when exposed to a particular RH.
 533 The prevention of moisture absorption is very beneficial applications like food packaging,
 534 especially for moisture-sensitive food products.



535 **Figure 8:** Moisture uptake of PVA and its nanocomposite films with CNC, GON and C:G
 536 (C:G-2:1, C:G-1:1 and C:G-1:2) hybrid nanofillers.

538 4. Conclusions

539 The reinforcing efficiency of graphene oxide nanosheets (GON) in polymer nanocomposites
 540 has been largely limited, because this water-dispersible nanofiller, at high loading level, tends
 541 to agglomerate within the polymer matrix. In this work we demonstrated that the combination
 542 of cellulose nanocrystals (CNC) and GON in a novel hybrid nanofiller (C:G hybrid) was
 543 highly effective to overcome the agglomeration phenomenon. After their combination, the
 544 CNC were found to be adsorbed on the surface of GON, forming a new network structure *via*
 545 hydrogen bonding interactions between the functional groups present in the surface of each
 546 nanomaterial. Three C:G hybrid nanofillers were prepared by varying the weight ratio of CNC
 547 and GON (2:1, 1:1 and 1:2) and their incorporation into PVA matrix was successfully
 548 achieved *via* solvent casting method leading to PVA-C:G-2:1, PVA-C:G-1:1 and PVA-C:G-
 549 1:2 nanocomposite films. Due to the strong interfacial interaction and the synergistic effect

550 generated from the combination of the two kinds of nanofillers (CNC and GON), the Young's
551 modulus, tensile strength and toughness of all the resulting PVA-C:G nanocomposites were
552 largely enhanced, and the elongation at break basically remained compared to pure PVA.
553 Simultaneously, the glass and melting temperatures as well as the moisture sorption of the
554 resulting nanocomposites were also improved. It was found also that the C:G hybrid
555 nanofiller containing a high amount of GON (C:G-1:2) showed a superior reinforcing
556 efficiency in the PVA nanocomposites. Comparatively, the results obtained for the C:G
557 hybrid nanofiller reinforced nanocomposite films were largely superior compared to those
558 found for nanocomposites containing either CNC or GON nanofillers, at the same loading
559 level. This finding was attributed to the synergistic effect of 1-D elongated CNC and 2-D
560 exfoliated GON, which improves the dispersion homogeneity by avoiding the agglomeration
561 phenomenon within the polymer, resulting in nanocomposites with enhanced properties
562 compared to those prepared from single nanofiller (CNC or GON). The preparation of this
563 novel hybrid nanofiller and its incorporation into the polymer matrix provided a novel method
564 to develop innovative materials, mainly by improving the mechanical properties of
565 nanocomposite films in applications where good strength, ductility and reduced moisture
566 absorption are required. Food packaging is one example of such applications.

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760 **Highlights**

- 761 - Cellulose nanocrystals (CNC) and graphene oxide (GON) were combined to get a novel
762 hybrid nanofiller
- 763 - 3D network microstructure was formed by the combination of CNC and GON two kinds of
764 nanomaterials
- 765 - Hybrid nanofiller was used to enhance the tensile properties of PVA nanocomposites
- 766 - Large increase of tensile properties of PVA was observed due to the synergistic effect

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