

Rheological, mechanical, thermal and electrical properties of UHMWPE/CNC composites

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(Article begins on next page)

32 **1. Introduction**

33 Ultra-high molecular weight polyethylene (UHMWPE) is an engineering polymer exploited in a wide
34 range of application fields including medical, textiles, agricultural, automotive and aerospace industry
35 (Gu 2015; Shanmugam et al. 2019; Sattari et al. 2014; Gürgen 2019; Rodrigues et al. 2019). The interest
36 in this polymer is mainly due to its intriguing properties, such as low density, ease of processing,
37 outstanding chemical stability, good electrical insulating properties, good mechanical and wear resistance
38 properties (Martínez-Morlanes et al. 2011; Hussain et al. 2020).

39 In recent years, considerable efforts have been made to further enhance UHMWPE properties, aiming at
40 widening its suitability for the formulation of energy devices (i.e. circuit boards, substrates, heat
41 exchangers, and electronic packaging) (Wang et al. 2018; Zhou et al. 2007; Gu et al. 2015; Zhou et
42 al.2012), for which the critical issues related to the heat removal are of fundamental importance. In this
43 context, materials with high heat dissipation characteristics and good electrical insulating properties have
44 paid an increasing attention, since economic lightweight solutions are needed (Zhou et al. 2015; Russo
45 et al. 2018).

46 The introduction of inorganic fillers into a polymer matrix is one of the most commonly methods
47 exploited for developing high performance materials. In literature, different fillers have been introduced
48 in UHMWPE with the aim of improving its mechanical properties and/or thermal conductivity. In this
49 context, UHMWPE-based composites containing zirconium particles (Plumlee and Schwartz 2009),
50 alumina toughened zirconia (Duraccio et al. 2019a, b), quartz (Xie et al. 2003), carbon nanotubes (Reddy
51 et al. 2018, Ruan et al. 2006; Xue et al. 2006) and graphite oxide (GO) (Suñer et al. 2015) have been
52 formulated through different processing methods. From a general point of view, regardless of the kind
53 of embedded particles, UHMWPE-based composites exhibited enhanced mechanical properties as
54 compared to the unfilled matrix. Besides, it has been demonstrated that the introduction of graphite
55 nanoplatelets (Feng et al. 2016), aluminum nitride (AlN) (Wang et al. 2016), boron nitride (BN) (Zhou
56 et 2007) and a combination of boron nitride and carbon nanotube (BN+CNT) (Guo et al. 2019) promotes
57 an enhancement of the UHMWPE thermal conductivity.

58 Cellulose nanocrystal (CNC) is a natural material obtained by the hydrolysis of cellulosic sources, and
59 the interest in its use as an organic reinforcement in polymer-based composites is considerably grown in
60 the last years. In fact, CNC can be obtained from renewable and abundant resources and has interesting
61 mechanical properties, coupled with biocompatibility and good thermal properties (Wang et al.2019;
62 Hamedi et al. 2014; Zhang et al. 2015). Several studies dealing with the evaluation of the mechanical
63 behavior of CNC-reinforced polymer nanocomposites shown that superior mechanical properties can be

64 achieved also for systems containing low CNC loadings, due to the intrinsic high stiffness of crystalline
65 cellulose and the high aspect ratio of the CNC particles (Dufresne 2012, Favier et al. 1995, Mariano et
66 al. 2014). The mechanical reinforcement mechanism is usually attributed to the formation of a three
67 dimensional rigid network, resulting from the percolation of the CNC rod-like particles, exhibiting higher
68 tensile modulus as compared to that of the individual nanocrystals (Bras et al. 2011). However, to fully
69 exploit the potential reinforcement provided by the CNC introduction, the right selection of the
70 processing method and the optimization of the operative conditions are of fundamental importance.
71 Despite many systems and possible applications have been exploited, the use of CNC as a filler for
72 UHMWPE to improve both the mechanical properties and thermal conductivity without modifying the
73 electrical behavior has not been studied yet. In this study, we prepared UHMWPE/CNC composites by
74 using different amounts of CNC (namely, 0.1, 2 e 5 wt.%) and different mixing procedures followed by
75 compression molding. The thermal, mechanical and electrical properties of UHMWPE/CNC composites
76 were thoroughly investigated. Additionally, the rheological properties and the effect of the CNC on the
77 polymer chain dynamics were also evaluated.

78

79 **2. Materials and Methods**

80 **2.1 Materials**

81 The materials used in this work were:

- 82 - Ultra-High Molecular Weight Polyethylene (UHMWPE, GUR4150), with an average particle size of
83 100 μm , and the molecular weight of $9 \times 10^6 \text{ g mol}^{-1}$, kindly supplied from Celanese Diversified
84 Chemical Co (China);
- 85 - Cellulose Nanocrystals, obtained by freeze-drying method, were purchased from CelluloseLab
86 (Canada). Cellulose Nanocrystals were obtained through acidic hydrolysis from different sources,
87 including cotton, softwood, hardwood and tunicate. The average particle sizes are: 10-20 nm width and
88 0.5-2 μm length. Before use, cellulose nanocrystals were dried in a vacuum oven at 80°C for 4h.

89

90 **2.2 Preparation of composites**

91 All the investigated composites were prepared through hot-compaction in a Carver laboratory press,
92 working at 160 °C under a pressure of 20 MPa for a total processing time of 7 min. First, UHMWPE/CNC
93 mixtures containing 0.1, 2 and 5 wt.% of CNC were prepared following two different approaches:

94 - Dry approach, in which UHMWPE powder was mechanically mixed at room temperature for 10
95 minutes with a proper amount of CNC particles. These last have been subjected to a preliminary ball
96 milling process (mCNC) by using a home-made ball mixer working at 30 rpm for 1h.

97 - Wet approach, in which 10 g of UHMWPE and a proper volume of CNC solution (5% w/v in deionized
98 water) were added to ethanol (80 ml) and stirred at room temperature until the complete evaporation of
99 the solvent was achieved. The so obtained mixtures were dried in a vacuum oven at 50 °C overnight. In
100 this case either as received CNC or mCNC particles subjected to ball milling process, at a speed of 30
101 rpm for 1h, were used.

102 All the produced composites were coded as: UHMWPE+xmCNC_dry, UHMWPE+xCNC_wet and
103 UHMWPE+xmCNC_wet, where x represents the CNC or mCNC content (wt.%).

104

105 **2.3 Characterizations**

106 An ARES (TA Instrument, USA) strain-controlled rheometer equipped with two parallel plates (plate
107 diameter = 25 mm) was used for studying the linear rheological behavior of UHMWPE-based systems.
108 The complex viscosity (η^*) of the unfilled polymer and its composites was measured through frequency
109 sweep tests from 0.1 to 100 rad/s at 200 °C. The strain amplitude was selected for each sample in order
110 to fall in the linear viscoelastic region.

111 LEO-1450VP Scanning Electron Microscope SEM (beam voltage: 20 kV) was used for the observation
112 of composite morphologies. Before testing, sample were fractured in liquid nitrogen and the obtained
113 surfaces were gold metallized.

114 X-ray powder diffraction (WAXD) patterns of CNC, unfilled UHMWPE and composites were obtained
115 with a Philips PW 1830 vertical diffractometer by using Bregg–Brentano geometry with Ni filtered Cu
116 $K\alpha$ radiation ($\lambda=0.15418$ nm) and a continuous scan of $0.02^\circ(\Delta 2\theta)/2s(\Delta t)$ in the range 5–45°. Elaboration
117 data was done by using the Rietveld analysis program FullProf (release 2011) (Rietveld 1967). The
118 crystallinity index of cellulose was evaluated using the empirical method described by Segal et al. (1959)
119 (equation 2):

$$120 \quad \chi = \frac{I_{200} - I_{am}}{I_{200}} \cdot 100 \quad (1)$$

121 where I_{am} is the minimum intensity between the peaks at 200 and 110 (at about 18°) and I_{200} is the
122 maximum intensity of the principal diffraction peak (200) (at $2\theta=22.6^\circ$ for cellulose I, and at $2\theta=21.7^\circ$
123 for cellulose II). This method does not allow assessing the absolute value of the crystallinity degree of
124 the material, but it is convenient for comparative purposes. The index of crystallinity χ_c of unfilled
125 UHMWPE and all formulated composites was calculated from the X-ray profiles as the ratio between

126 the intensity of the crystalline phase and the total diffraction intensity of the sample. The intensity of the
127 crystalline phase was obtained through the subtraction of the amorphous phase corrected for the real
128 amount of UHMWPE in the composite. The profile of amorphous phase was approximated with an
129 spectrum obtained by averaging the profiles of UHMWPE melted at 180, 190 and 200 °C. The following
130 equation (2) was used, for the calculation of the crystallinity degree:

$$131 \quad x_c = \frac{I_{TOT} - [I_{am(PE)} * m(PE)]}{I_{TOT}} * 100 \quad (2)$$

132 where $m(PE)$ is the mass fraction of PE in the composites and I_{TOT} is the total intensity of the diffraction
133 spectrum.

134 The mechanical properties of all investigated materials were evaluated through tensile tests performed
135 on compression-molded dumbbell specimens ($50 \times 3.15 \times 1 \text{ mm}^3$) using an Instron dynamometer
136 (Instron® 5966) and following the ASTM D638-03 standard. The ratio between the drawing rate and the
137 initial length was fixed equal to 0.1 mm/(mm·min) for the measurement of the Young's modulus; for the
138 stress-strain curves and the determination of stress and strain at break and at yield, the ratio was fixed
139 equal to 10 mm/(mm·min). The reported curves and the main mechanical parameters were averaged over
140 six independent measurements for each type of CNC-reinforced UHMWPE nanocomposites.

141 The thermal and thermo-oxidative stability of CNC particles, unfilled UHMWPE and composites was
142 evaluated using a Pyris1TGA apparatus (Perkin Elmer, USA) (experimental error: $\pm 0.5 \text{ wt.}\%$, $\pm 1 \text{ }^\circ\text{C}$). 10
143 mg of samples were placed in alumina pans and heated at 10 °C/min from 50°C to 700 °C, under both
144 N_2 and air flow (35 and 25 mL/min, respectively). $T_{10\%}$, $T_{50\%}$ (i.e., the temperatures, at which 10% or
145 50% weight loss, respectively, occurs), and T_{max} values (i.e. The temperature at which the rate of weight
146 loss is at a maximum) were calculated; besides, the final residue at 600 °C was measured.

147 The thermal conductivity of unfilled UHMWPE and its composites was measured by means of a TPS
148 2500S Hot Disk instrument (AB Corporation-Göteborg, Sweden), by using the Transient Plane Source
149 (TPS) method (Gustavsson et al. 1994). A silicon oil bath (Haake A40, Thermo Scientific Inc., Waltham,
150 MA USA), equipped with a temperature controller (Haake AC200, Thermo Scientific Inc., Waltham,
151 MA, USA) was used for controlling the test temperature ($23.00 \pm 0.01 \text{ }^\circ\text{C}$). The bulk measurements were
152 performed by putting a Kapton sensor (radius 3.189 mm) between two similar slabs of material (30×30
153 $\times 3 \text{ mm}^3$). The thermal conductivity was obtained by recording the change temperature recorded when
154 the sensor supplied a heat pulse of 0.03 W for 2 seconds to the sample.

155 The direct current (DC) electrical resistivity measurements were carried out using a setup in accordance
156 with the ASTM D257 standard. More information is given in the supplementary section (see Figs. 7 and

157 8). In brief, the setup consists of a pico-ammeter (model 6517B; Keithley Instruments, Cleve-land, Ohio,
158 USA) connected to Keithley 8009 two-probe test fixture. The measurement of the volume resistivity was
159 performed in the presence of a guard electrode that makes it possible to selectively measure the current
160 flowing through the sample reducing the possibility of noise and interference of a sample (Blythe 1984).
161 The electrical connections between the measuring instrument and the sample were stable and repeatable.
162 The measurements were performed with the same bulk specimens used for thermal conductivity at
163 $23.0\pm 0.3^{\circ}\text{C}$. The reported results represent an average of three different specimens for each formulation.
164

165 **3. Results and Discussion**

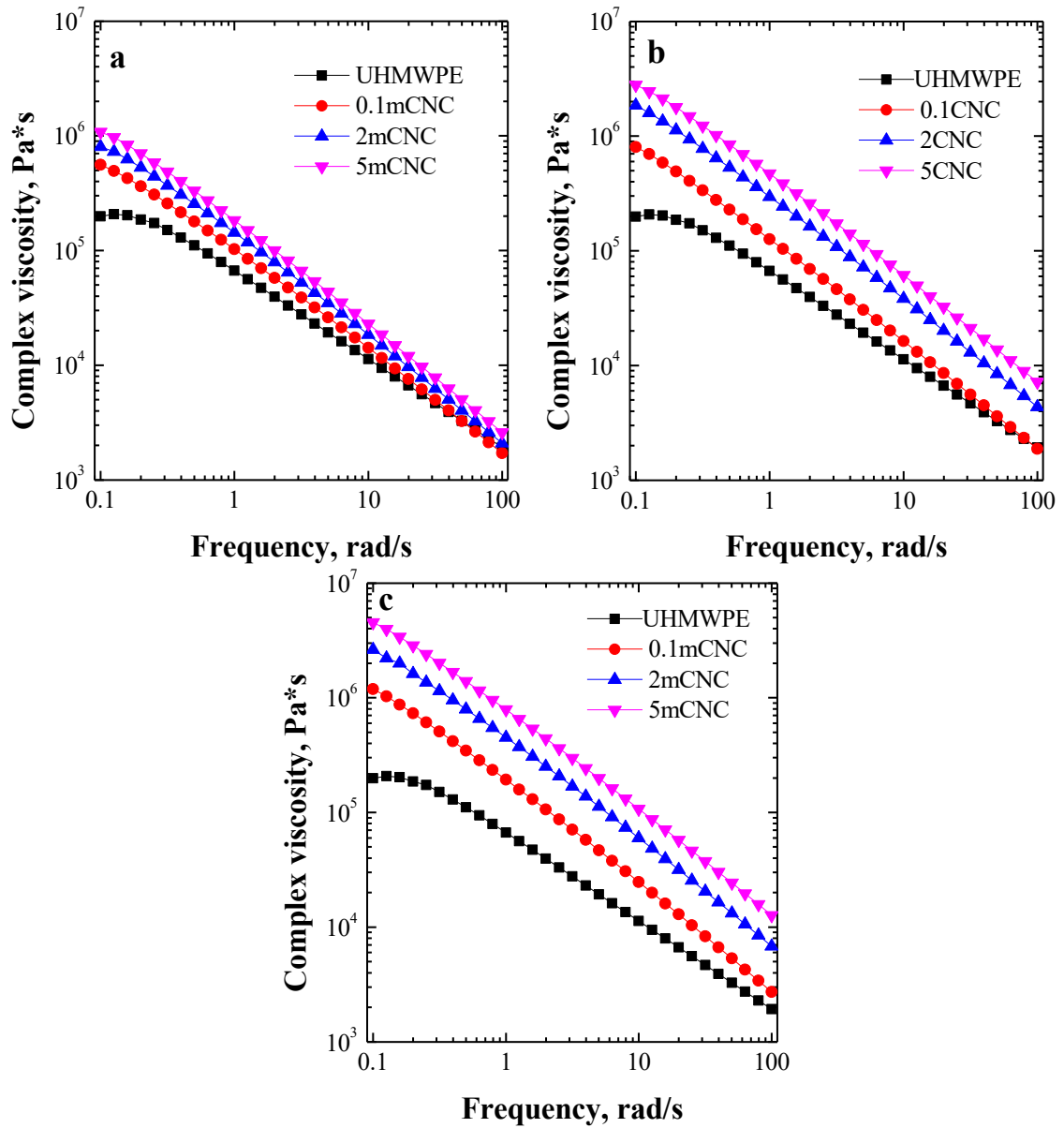
166 In Fig. 1, the complex viscosity as a function of frequency for all the investigated composites is reported
167 and compared to that of unfilled matrix.

168 UHMWPE exhibits power-law behaviour, showing a Newtonian plateau only at the lowest investigated
169 frequencies. The significant non-Newtonian behaviour of unfilled UHMWPE can be attributed to the
170 very high molecular weight of the matrix, whose macromolecules are characterized by a large density of
171 entanglements hampering the relaxation of the polymer macromolecules (Dintcheva et al. 2016). All the
172 CNC-containing composites, regardless of the adopted processing method, show higher complex
173 viscosity values as compared to unfilled matrix, with a progressive increment according to the increased
174 CNC loadings. However, this increment is large at 0.1 wt.% and becomes moderate for higher CNC
175 concentration. It is well known that the rheological behaviour of the CNC-containing nanocomposites is
176 strictly related to their morphology that, in turn, depends on the selected processing method. In the
177 present study, the UHMWPE nanocomposites were obtained through hot-compaction and, as
178 demonstrated by morphological analyses reported below, they show a peculiar morphology that
179 significantly differs from that usually observed for CNC-containing nanocomposites obtained through
180 melt mixing or solvent casting. In fact, in these last cases, a uniform dispersion of the CNC particles
181 within the polymer matrix is typically obtained, and the introduction of increasing amounts of fillers
182 causes the formation of a percolated network that significantly modify the rheological response of the
183 polymer matrix, as widely reported in the literature (Ching et al. 2016; Shojaeiarani et al, 2021). In the
184 UHMWPE/CNC nanocomposites here investigated, the introduction of 0.1 wt.% of CNC particles causes
185 the formation of CNC-rich zones surrounding the UHMWPE grains and the achieved morphology
186 induces an increase of the complex viscosity in the low frequency region, due to the restrain of the
187 dynamics of the polymer macromolecules. A further increase of the CNC content does not correspond to

188 a remarkable rise of the polymer/filler interfacial area; therefore, the enhancement of the complex
189 viscosity values as a function of the CNC amount is very limited.

190 Finally, it worthwhile to underline that, the achievement of higher viscosity values is more pronounced
191 in the low frequency region, indicating that the embedded CNC particles cause a further restriction of
192 the macromolecular motion of UHMWPE chains, hindering their complete relaxation. Conversely, the
193 convergence of the viscosity curves at higher frequencies suggests a negligible effect of CNC on the
194 short-range dynamics of polymer chains. Furthermore, the modification of the UHMWPE rheological
195 behavior resulting from CNC introduction is more pronounced in composites formulated using the wet
196 approach, suggesting the formation of a larger polymer/particles interfacial area with respect to the
197 materials produced through dry method.

198 Fig. 2 reports the storage modulus as a function of frequency for unfilled UHMWPE and all CNC-
199 containing composites obtained through the different methods. Similarly to what observed for the
200 complex viscosity, the introduction of increasing amounts of CNC particles induces a progressive
201 enhancement of the values of the modulus with respect to the unfilled matrix. Also in this case, the
202 embedded particles are able to affect mainly the long-range dynamics of UHMWPE macromolecules,
203 whose response is recorded at low frequencies. In particular, the storage modulus curves of all
204 nanocomposites exhibited lower slope in the terminal region as compared to the unfilled matrix,
205 suggesting the achievement of a solid-like rheological response due to the establishment of polymer/filler
206 interactions in the interfacial region, which induce a restrain of the polymer chain dynamics.

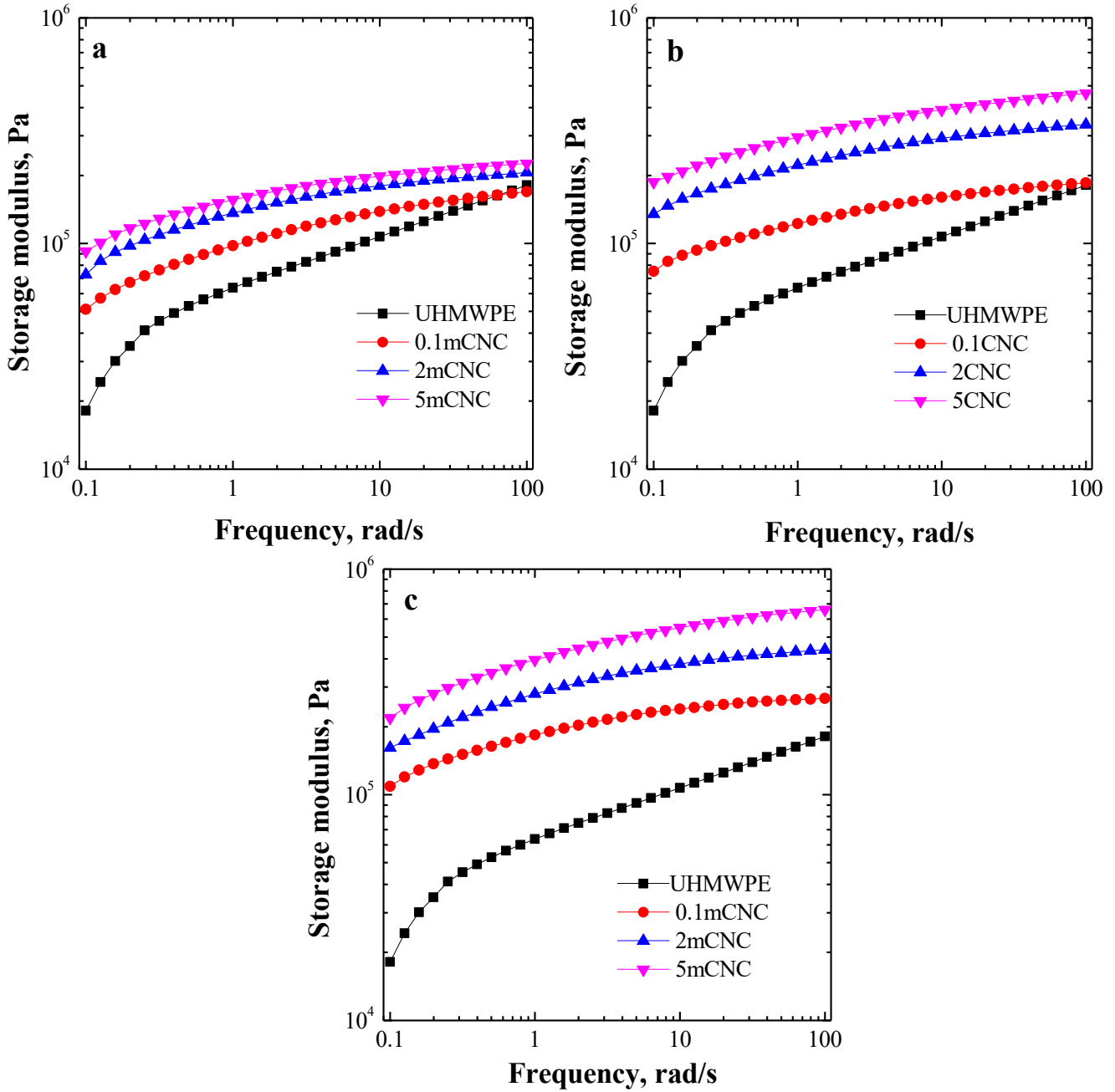


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208

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Fig. 1 Complex viscosity as a function of frequency for (a) UHMWPE+mCNC_{dry}, (b) UHMWPE+CNC_{wet} and (c) UHMWPE+mCNC_{wet} composites

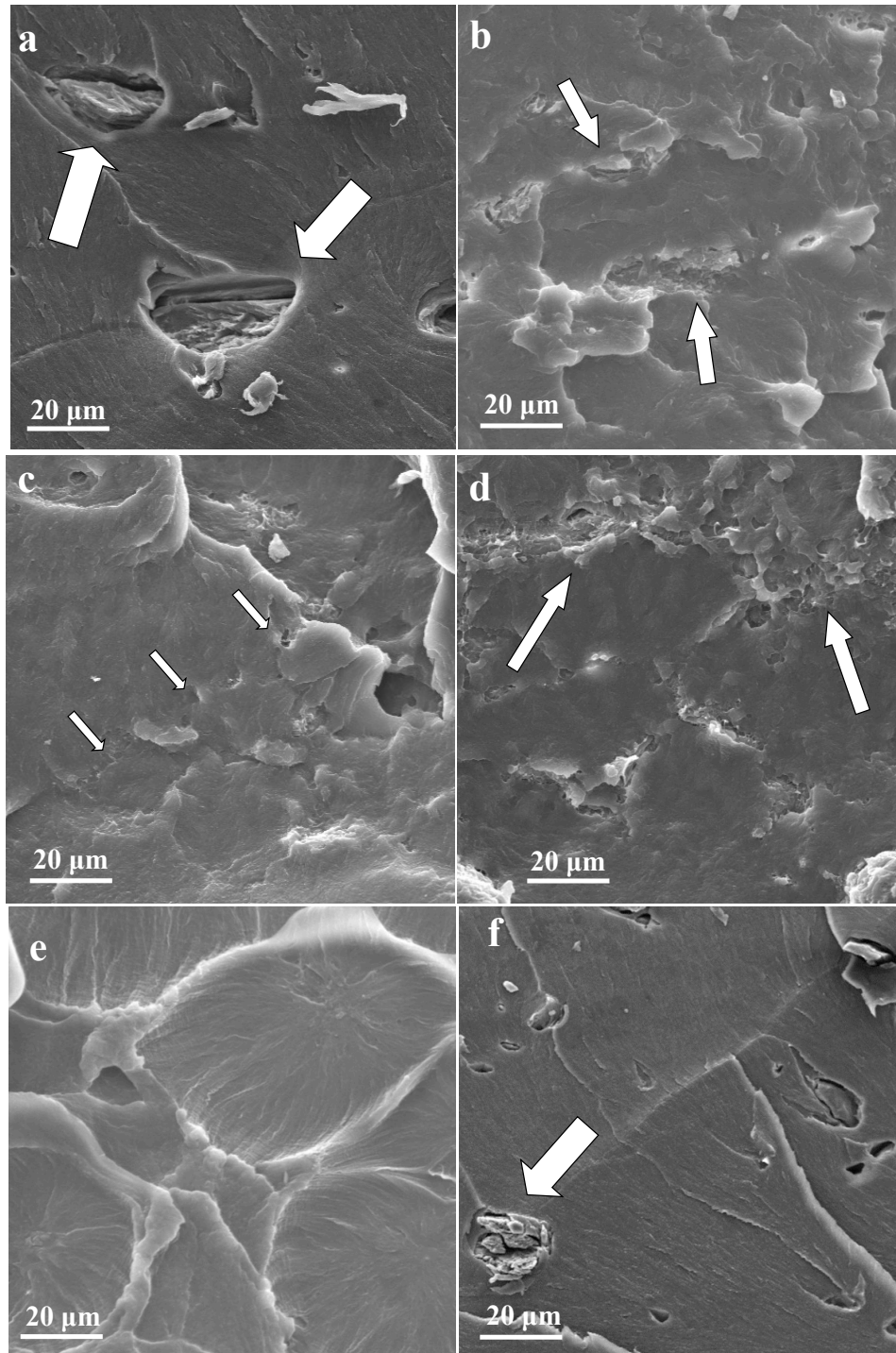


210
 211 **Fig. 2** Storage modulus as a function of frequency for (a) UHMWPE+mCNC_dry, (b)
 212 UHMWPE+CNC_wet and (c) UHMWPE+mCNC_wet composites
 213

214 To support the results coming from rheological characterization, morphological analysis was performed.
 215 Fig. 3 shows the typical SEM micrographs of all the composites containing 2 wt.% of CNC. In the
 216 composites obtained through dry method, the embedded particles are uniformly dispersed within the host
 217 matrix, notwithstanding the presence of some agglomerates, especially for the systems containing high
 218 CNC loadings. Besides, the agglomerates appear detached from the matrix surface, suggesting the

219 occurrence of weak interactions between the filler and UHMWPE. Differently, the composites obtained
220 through wet method present a more regular morphology, involving the preferential segregation of the
221 embedded particles within the interfacial region between UHMWPE grains. This peculiar microstructure,
222 which has already been reported in literature for UHMWPE-based composites (Ren et al. 2016), is a
223 direct consequence of the exploited preparation method. In particular, during composite preparation,
224 CNC particles cover the polymer particles in the initial UHMWPE/CNC powder mixture, remaining at
225 the boundaries between UHMWPE grains during the hot compression. The different morphology
226 obtained for composites formulated through wet method can be attributed to the beneficial effect of the
227 dispersion of both CNC and UHMWPE particles in the solvent, which facilitates the distribution of CNC
228 particles around UHMWPE grains, promoting the achievement of a segregated microstructure. For
229 UHMWPE+mCNC_wet composites, the dispersion of filler is better when 0.1 wt.% of CNC is used.
230 This is clearly depicted in the SEM micrograph reported in Fig. 3c.
231 Regarding UHMWPE+CNC_wet (no-ball milled composites) systems, the distribution of filler around
232 UHMWPE grains is not always uniform and well detectable as shown in Fig. 3e, and the presence of
233 some agglomerates at the micrometric scale can be observed (Fig. 3f).

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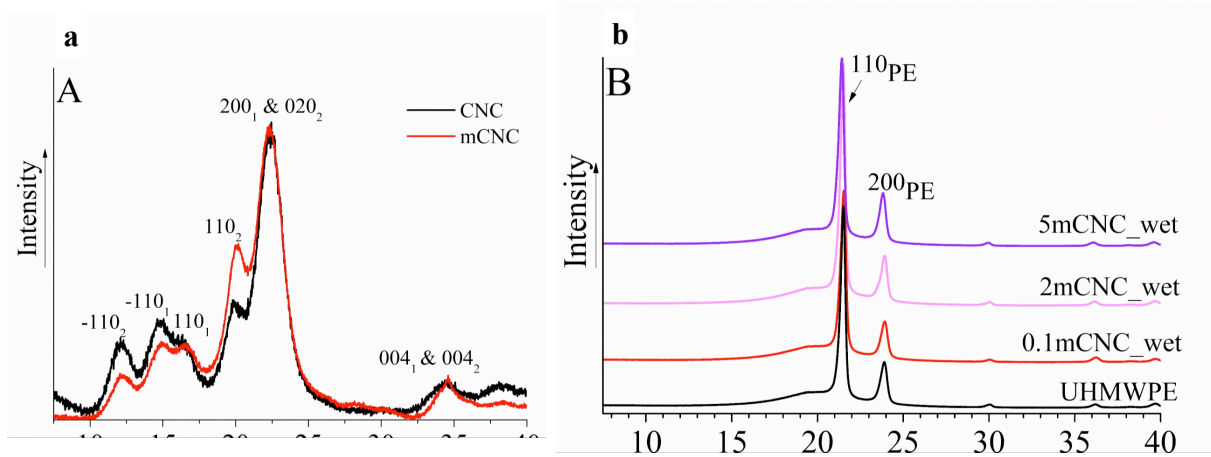
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239

Fig. 3 SEM micrographs of (a) UHMWPE+2mCNC_dry, (b) UHMWPE+2mCNC_wet, (c) UHMWPE+0.1mCNC_wet, (d), (e) and (f) UHMWPE+2CNC_wet composites. White arrows indicate the presence of CNC

240 Fig. 4a reports the diffraction patterns of commercial and ball milled cellulose. The curves have been
241 corrected for the background signal and normalized to the most intense peak of the spectra (i.e. 200₁ &
242 020₂ centered at about 22.3°).



243

244 **Fig. 4** WAXD pattern of a) as obtained (CNC), and ball milled (mCNC) cellulose; b) UHMWPE and
245 UHMWPE composites obtained with a wet approach
246

247 It is well known that cellulose nanocrystals include two polymorphs, namely cellulose I and II (Garvey
248 et al. 2005, French and Santiago 2013). The peaks at $2\theta = 12.2^\circ$ and 19.7° are assigned to -110 and 110
249 crystalline planes of cellulose II (Nishiyama et al. 2002). Peaks at $2\theta = 14.7^\circ$ and 16.5° are due to the
250 diffraction of the -110 and 110 crystalline planes of cellulose I (Ago et al. 2002). The 200 (at $2\theta = 22.3^\circ$)
251 and 004 (at $2\theta = 34.5^\circ$) reflections belong to cellulose I and overlap with the 020 and 040 reflections of
252 cellulose II. The spectra in Fig. 4a clearly indicate that the cellulose used in this work is a mixture of the
253 two forms. Besides, ball milling does not induce any phase transformation as sometimes reported in
254 literature (Ago et al. 2002): in the normalized curves of ball milled cellulose, there is not the same
255 (positive or negative) variation of peak intensity relative to form I as regards to that of form II. This
256 means that ball milling has only modified the preferential orientation of some crystallographic planes
257 with respect to others.

258 The crystallinity index (χ) of the cellulose was measured according to Segal equation (equation 1). This
259 method for calculating the crystallinity index provides reliable relative crystallinity for comparison
260 purposes, as it assumes that the amount of the crystalline region is represented by the intensity of the
261 highest diffraction peak and the amount of amorphous region is represented by the minimum intensity
262 between the 200₁ & 020₂ peaks and 110₂. Though other methods, reported in literature, are more realistic
263 (Thygesen et al. 2005), the Segal approach is very straightforward and quick to use. The crystallinity

264 index of cellulose found by following the Segal method is 89% for the as obtained cellulose and 82% for
 265 the ball milled cellulose. The decrease of crystallinity due to the mechanical treatment is well documented
 266 in literature (Schwanninger et al. 2004).

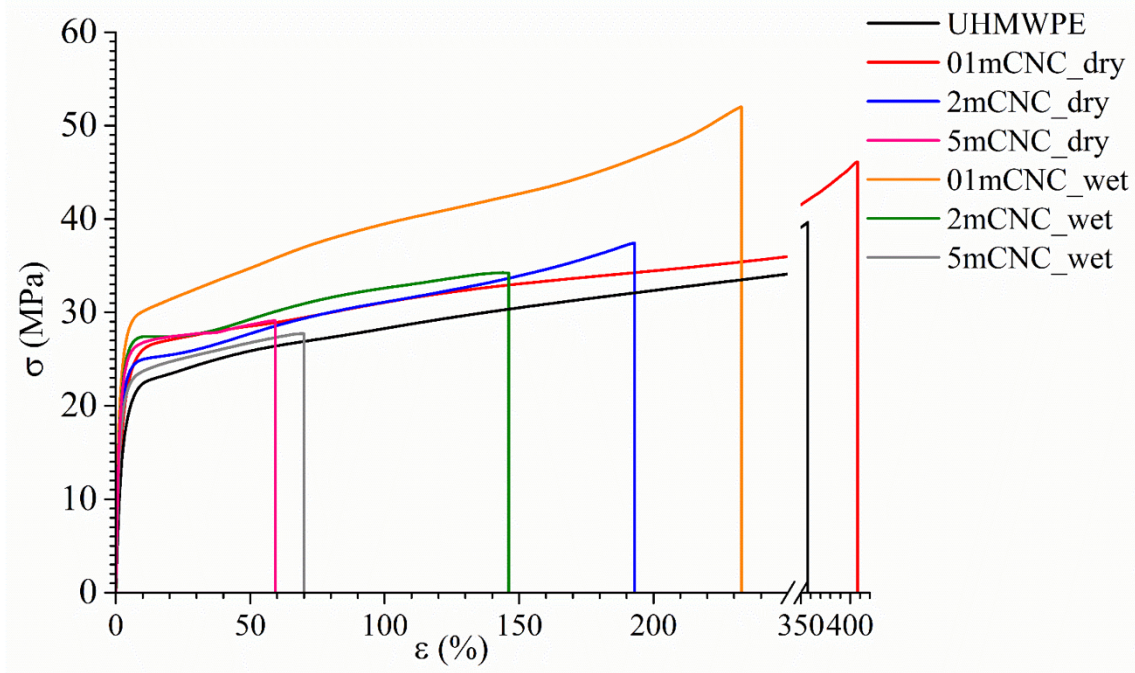
267 Fig. 4b reports the typical diffraction patterns of some UHMWPE/CNC composites. UHMWPE and all
 268 the composites, regardless of the mixing technique, crystallize in the orthorhombic form of PE as
 269 evidenced by the intense peaks at about $2\theta = 21, 24$ and 36° corresponding to the 110, 200 and 020
 270 reflections, respectively (Bunn 1939). In the diffraction profiles, the reflections of Form I and II of
 271 cellulose are not visible due to both the overlapping with PE peaks and to the limited CNC loading in the
 272 composites. As shown in Table 1, the crystallinity of the composites obtained from the formula (2) is
 273 always higher than that of pure UHMWPE. This is probably due to the fact that CNCs act as a
 274 heterogeneous nucleating site for crystallization, improving the crystallinity of UHMWPE. The highest
 275 increase (i.e. 22%) can be observed for UHMWPE/5mCNC_wet with a x_c of 66%.

Table 1. Crystallinity index (χ (WAXS)), Young modulus (E), yield stress (σ_y), stress (σ_b) and strain (ϵ_b) at break of UHMWPE and its composites.

	$\chi, \%$	E, MPa	σ_y, MPa	σ_b, MPa	$\epsilon_b, \%$
UHMWPE	54	782 ± 62	22 ± 3	38 ± 5	332 ± 66
UHMWPE+0.1CNC_wet	59	1141 ± 223	26 ± 6	39 ± 3	207 ± 40
UHMWPE+2CNC_wet	61	1202 ± 153	22 ± 8	26 ± 2	87 ± 27
UHMWPE+5CNC_wet	63	1650 ± 217	24 ± 4	8 ± 3	45 ± 12
UHMWPE+0.1mCNC_dry	57	962 ± 72	26 ± 4	46 ± 2	404 ± 17
UHMWPE+2mCNC_dry	59	1284 ± 57	24 ± 1	36 ± 3	187 ± 28
UHMWPE+5mCNC_dry	61	1736 ± 28	26 ± 2	29 ± 1	65 ± 7
UHMWPE+0.1mCNC_wet	61	1428 ± 83	30 ± 2	48 ± 4	227 ± 8
UHMWPE+2mCNC_wet	63	1500 ± 66	27 ± 2	36 ± 3	149 ± 15
UHMWPE+5mCNC_wet	66	1533 ± 12	23 ± 1	29 ± 1	70 ± 17

276
 277 Fig. 5 shows the typical stress–strain curves of the UHMWPE and UHMWPE/CNC composites; the
 278 tensile properties are collected in Table 1. As expected, neat UHMWPE after yielding draws with strain
 279 hardening effect and finally breaks at a quite long deformation (Xie et al. 2003). As shown in Fig. 4,
 280 different CNC loadings and different mixing conditions exert different effects on the tensile properties
 281 of the composites. An enhancement of Young’s modulus is observed for all the investigated composites:
 282 more specifically, the higher the CNC loading, the stiffer is the composite. This is in agreement with the

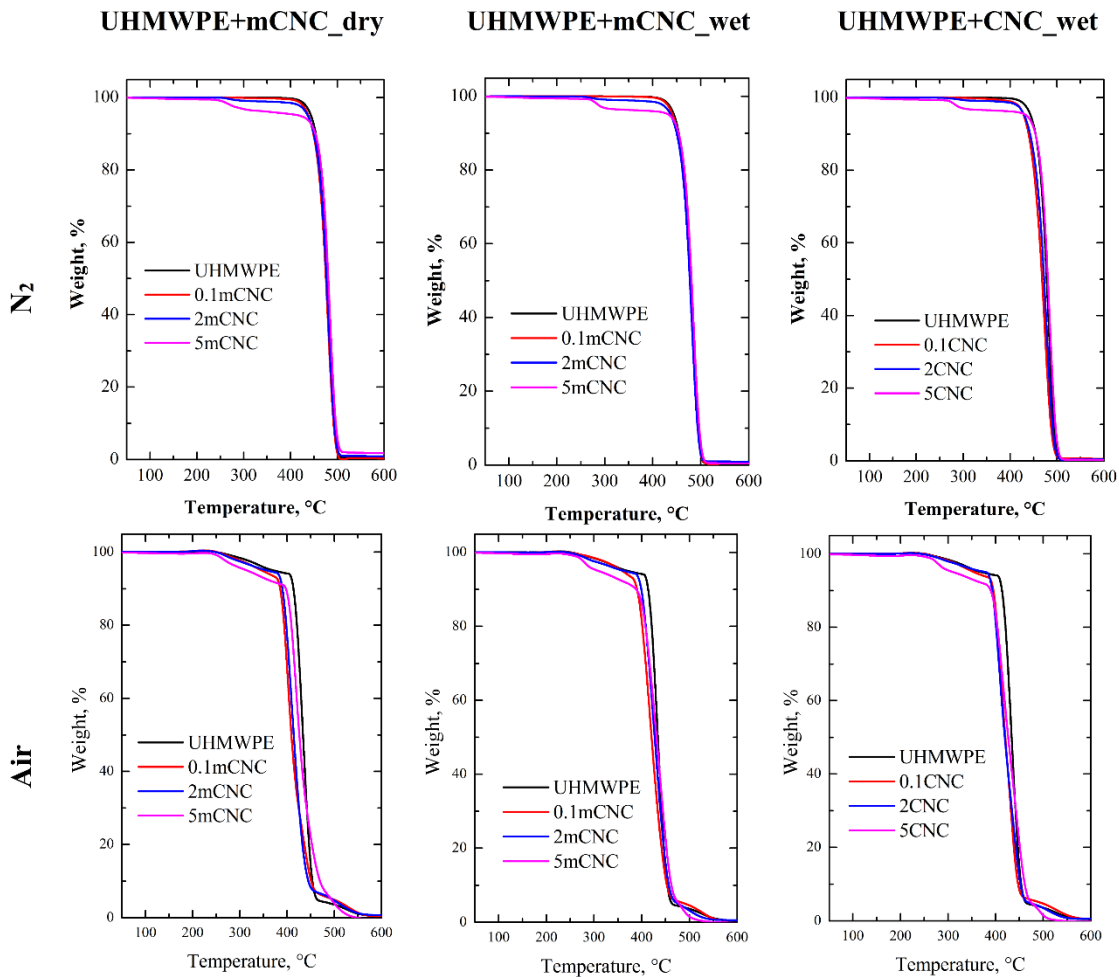
283 results found for other UHMWPE composites and can be ascribed to both their higher crystallinity degree
284 with respect to that of unfilled polymer and to the reinforcement effect provided by the filler (Xie et al.
285 2003; Suñer et al. 2015; Lombardo et al. 2016; Dorigato et al. 2013).
286



287
288 **Fig. 5** Stress-strain curves of UHMWPE and UHMWPE/CNC composites
289

290 Besides, though yielding strength in composites is always higher than that of neat UHMWPE, the
291 ultimate tensile strength reaches a maximum corresponding to 0.1 wt.% of CNC and then decreases,
292 becoming lower than that of neat UHMWPE for composites obtained in wet conditions. The same
293 behaviour is shown by the elongation at break for the composites obtained in dry conditions, whereas for
294 the other methods it continues to decrease with increasing CNC content and is always lower with respect
295 to that of unfilled UHMWPE. Again, the results are in good agreement with those reported for other
296 UHMWPE composites (Chen et al. 2012; Suñer et al. 2015, Feng et al. 2016). Wang et al. (2016)
297 observed that CNC-doped UHMWPE composites exhibit higher ultimate tensile strength than that of
298 neat UHMWPE, which starts to decrease beyond 2 wt.%. Analogously, Pang et al. (2015) found that the
299 tensile strength achieved an optimal value at a specific GO content: too high or too low GO loadings
300 were found to decrease the composite performance. As reported in the literature, the increase in the
301 elongation at break, found for composites obtained in dry conditions, can be generally explained through
302 a well-known failure mode characterized by debonding at the matrix–particle interface in polymer

303 composites, which causes the formation of massive voids that coalesce during matrix fibrillation (Michler
 304 and Kausch-Blecken von Schmeling 2013; Khumalo et al. 2011). This mechanism of failure in polymer
 305 composites happens in general at low filler amounts because the voids have small dimensions (Michler
 306 and Kausch-Blecken von Schmeling 2013; Khumalo et al. 2011; Di Maro et al. 2021). SEM analysis
 307 (Fig. 3 a) evidences that polymer-filler interface is very poor in UHMWPE/CNC_dry composites, hence
 308 supporting this hypothesis.



309
 310

311 **Fig. 6** Thermogravimetric curves for unfilled UHMWPE and all formulated CNC-containing
 312 composites, obtained both in N₂ and air

313

314 By comparing the composites obtained by wet method, two observations are noteworthy. The first one
 315 is that the reduction of size and crystallinity of CNC particles when subjected to ball milling (crystallinity
 316 mCNC < crystallinity CNC) does not influence the mechanical behavior of UHMWPE composites. Then,
 317 UHMWPE+xmCNC_wet (ball milled CNC) composites have a more uniform distribution of filler

318 around UHMWPE grains than that of UHMWPE+xCNC_wet (no-ball milled) counterparts, hence
 319 providing more reproducible results. The higher standard deviation in the mechanical parameters of
 320 UHMWPE+xCNC_wet with respect to the other systems can be attributed to inhomogeneous distribution
 321 of the filler around polymer grains.

322 The melting and crystallization temperatures and crystallinity degree of unfilled UHMWPE and of all
 323 the formulated composites were assessed through DSC analyses. The obtained results (reported in Table
 324 3 in Supplementary material) documented a negligible effect of the embedded CNC particles on the
 325 characteristic temperatures of the polymer matrix, irrespective of the filler content and processing method
 326 used. Besides, the introduction of CNC particles induced an enhancement of the crystallinity degree as
 327 compared to the unfilled matrix, further supporting the results from XRD measurements.

328 Fig. 6 shows the typical TG curves obtained in nitrogen and air atmospheres for unfilled UHMWPE and
 329 its composites (dTG curves are reported in Fig. 9); furthermore, $T_{10\%}$, $T_{50\%}$, T_{max} , and the final residues
 330 at 600 °C in both atmospheres are collected in Table 2. TG and dTG curves of CNC particles are reported
 331 in the Supplementary material (Fig. 10).

332

Table 2. Results from TG analyses for UHMWPE and its composites

	Filler loading [wt.%]	Atmosphere: N ₂				Atmosphere: air			
		T _{10%} [°C]	T _{50%} [°C]	T _{max} [°C]	Residue @600°C [wt.%]	T _{10%} [°C]	T _{50%} [°C]	T _{max} [°C]	Residue @600°C [wt.%]
UHMWPE	0.00	454	478	483	0.6	407	434	433	0.5
mCNC_dry	0.10	449	476	482	0.3	379	411	407	0.4
	2.00	449	477	482	0.9	385	415	412	0.7
	5.00	449	480	483	1.2	390	427	423	0.8
CNC_wet	0.10	436	467	482	0.6	389	421	420	0.4
	2.00	440	471	481	0.5	387	420	414	0.5
	5.00	450	479	484	0.5	384	427	423	0.6
mCNC_wet	0.10	450	477	478	0.6	384	421	420	0.5
	2.00	448	476	480	0.5	394	427	426	0.6
	5.00	450	479	486	0.6	384	431	433	0.5

333

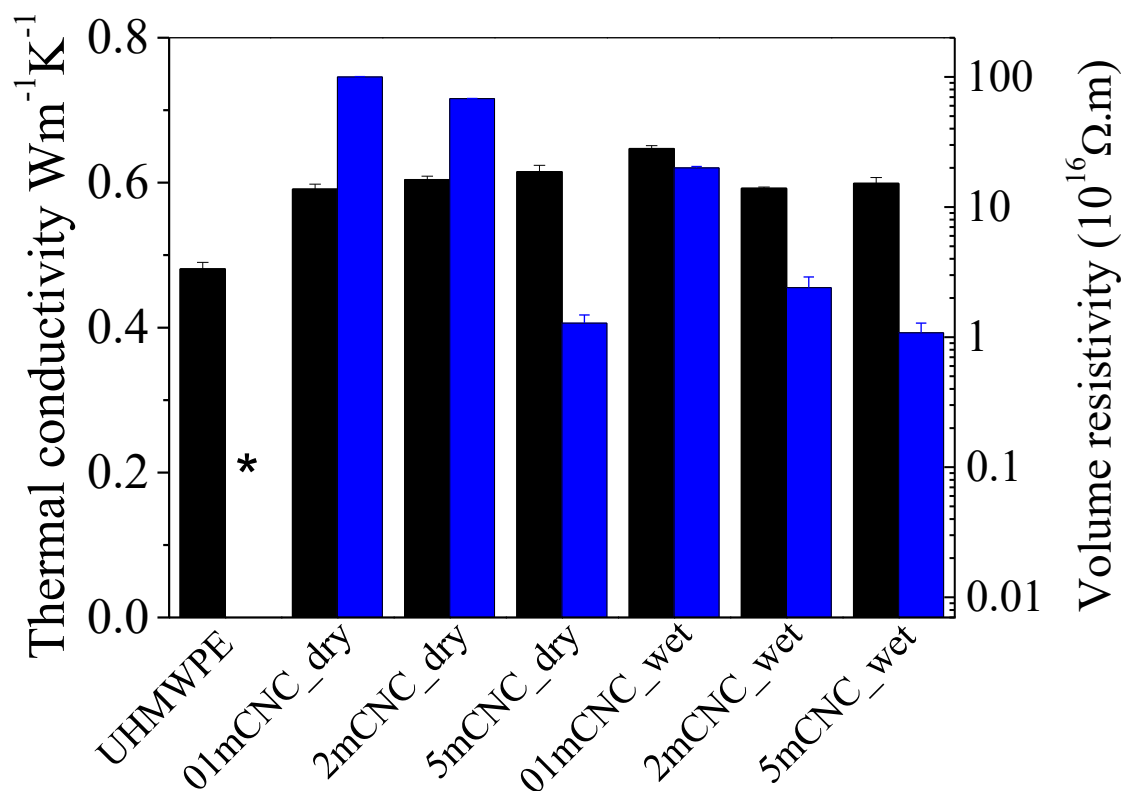
334

335 In inert atmosphere, degradation occurs in a single step for all the systems investigated. Furthermore, the
 336 presence of the CNC particles, irrespective of the loading and of the method used for the preparation of
 337 the composites, did not significantly affect the thermal stability of UHMWPE, since the typical
 338 temperatures characterizing the thermal stability of unfilled matrix are almost unchanged in all composite

339 systems. In air, the embedded CNC particles caused a slight worsening of the thermo-oxidative stability
340 of polymer matrix, recognisable in an anticipation of the degradation onset and of the maximum
341 degradation temperature. It is worthwhile to underline that the improved stability of mCNC particles,
342 attributed to the re-arrangement of the sulphated groups usually present within CNC structure as a result
343 of the treatment with sulfuric acid during the preparation of cellulose nanocrystals, induced by the ball
344 milling treatment (Kargarzadeh et al 2012; Roman and Winter 2004), does not affect the thermo-
345 oxidative stability of the composites.

346 Fig. 7 shows the thermal conductivity and the volume resistivity of UHMWPE and its composites
347 prepared in dry and wet conditions with different mCNC loadings. UHMWPE+xmCNC_wet composites
348 (obtained by wet method but using the as obtained CNC) behave similarly to UHMWPE+xmCNC_wet.
349 However, considering the high sensitivity of resistivity measurements, results for
350 UHMWPE+xmCNC_wet scatter over a wide range (as already observed for the mechanical behavior),
351 confirming the poor distribution of CNC around UHMWPE grains. For this reason, results are not
352 reported here.

353 The thermal conductivity of UHMWPE is equal to $0.481 \text{ Wm}^{-1}\text{K}^{-1}$, in accordance with the values reported
354 in the literature (Ren et al. 2016; Xue et al. 2006). In the composites, the thermal conductivity coefficient
355 is always higher than that of neat polymer and varies with the composition and the mixing procedure.
356 More in detail, in the dry method, the thermal conductivity slightly increases by increasing the mCNC
357 amount and reaches the value of $0.615 \text{ Wm}^{-1}\text{K}^{-1}$ when the amount of mCNC is 5wt.% (+28% increase
358 with respect to unfilled polymer matrix). In the wet method, there is not a proportional increase of thermal
359 conductivity with mCNC amount, but the best performance (+34%) is obtained when 0.1 wt.% of mCNC
360 is used. In literature are reported some significant improvement of thermal conductivity for UHMWPE
361 composites respect to neat polymer. For example, Guo et al. (2019) found that the thermal conductivity
362 of UHMWPE reached $2.38 \text{ W m}^{-1}\text{K}^{-1}$ when 40 wt.% of boron nitride (BN) and 7 wt.% of carbon
363 nanotube were added to neat UHMWPE. Wang et al. (2020) found a thermal conductivity of 9.99 W
364 $\text{m}^{-1}\text{K}^{-1}$ for UHMWPE/BN 68.4/21.6 wt.% composites obtained by a heat-treatment powder mixing
365 method. Despite the difference with respect to the systems reported in literature, the proposed
366 UHMWPE/CNC composites show two advantages: the low amount of filler used for preparing the
367 composites and the organic nature of the filler (CNC), which is a key element for innovative devices in
368 the field of green technologies. This suggests to continue the work in this field, exploring different
369 polymer matrices and preparation methods.



370

371 **Fig. 7** Thermal conductivity (black bars) and volume resistivity in log scale (blue bars) of composites

372

373 Fig. 7 also shows the volume resistivity for mCNC composites, which slightly decreases with increasing
 374 mCNC content in the samples prepared with either dry or wet method. In particular, for neat UHMWPE
 375 it was not possible to detect the value with the instrumentation used, as it exceeded the maximum
 376 measurable value (i.e. $10^{18} \Omega \cdot m$). However, the volume resistivities were in the range from $1.0 \cdot 10^{18}$ to
 377 $1.28 \cdot 10^{16} \Omega \cdot m$, for the composites prepared by dry method and from $2.0 \cdot 10^{17}$ to $1.08 \cdot 10^{16} \Omega \cdot m$ for those
 378 prepared by wet method. The slight decrease of the volume resistivity by increasing mCNC amount can
 379 be attributed to lower electric resistivity of the cellulose as compared to UHMWPE, as already observed
 380 for other systems (Xue et al. 2006; Blythe 1984). The better distribution of the filler around UHMWPE
 381 grains in the polymer matrix is also responsible for the lower values of volume resistivity in the
 382 composites obtained by wet method with respect to those obtained by dry method. These values ($\sim 10^{16}$
 383 $\Omega \cdot m$), however, still demonstrate that composites have excellent electrical insulation properties that
 384 suggest the application of these materials as electrical insulators.

385

386

387 **Conclusions**

388 In this work, UHMWPE/CNC composites have been prepared by using three different mixing
389 procedures, either dry or wet, followed by compression molding. On the basis of the experimental results
390 obtained for the composite systems containing up to 5 wt.% of CNC, the following conclusions can be
391 drawn:

- 392 i) Ball milling treatment, used for reducing the size of CNC particles, is fundamental for obtaining
393 UHMWPE composites showing a uniform distribution of the filler and reproducible results.
- 394 ii) CNC is responsible for the increase of polymer stiffness due to its nucleating effect. Ultimate
395 tensile strength achieves its maximum value for the composites containing 0.1 wt.% of CNC, and then
396 progressively decrease with increasing the particle content.
- 397 iii) Composites prepared through wet method show a uniform distribution of mCNC particles around
398 UHMWPE grains, which favors the formation of a segregated microstructure, responsible for the
399 enhancement of the thermal conductivity and for the slight decrease of the electrical volume resistivity.
400 However, the minimum volume resistivity values are not below $10^{16} \Omega \cdot m$, hence indicating that the
401 designed composites have excellent electrical insulation properties.

402

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408 **Data Availability:** Raw data can be obtained from the authors on request.

409 **Supporting Information:** Additional experimental details and Fig.s.

410

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