

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

*Original*

Rheological, mechanical, thermal and electrical properties of UHMWPE/CNC composites / Duraccio, D., Arrigo, R., Strongone, V., Capra, P.P., Malucelli, G.. - In: CELLULOSE. - ISSN 0969-0239. - ELETTRONICO. - 28:17(2021), pp. 10953-10967. [10.1007/s10570-021-04227-5]

*Availability:*

This version is available at: 11583/2937147 since: 2021-11-11T17:55:20Z

*Publisher:*

Springer

*Published*

DOI:10.1007/s10570-021-04227-5

*Terms of use:*

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

Springer postprint/Author's Accepted Manuscript

This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: <http://dx.doi.org/10.1007/s10570-021-04227-5>

(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  $\mu\text{m}$ , 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  $\mu\text{m}$  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 ( $\eta^*$ ) 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  $\chi_c$  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<sub>2</sub> 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  $T_{\text{max}}$  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 ( $30 \times 30$   
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**

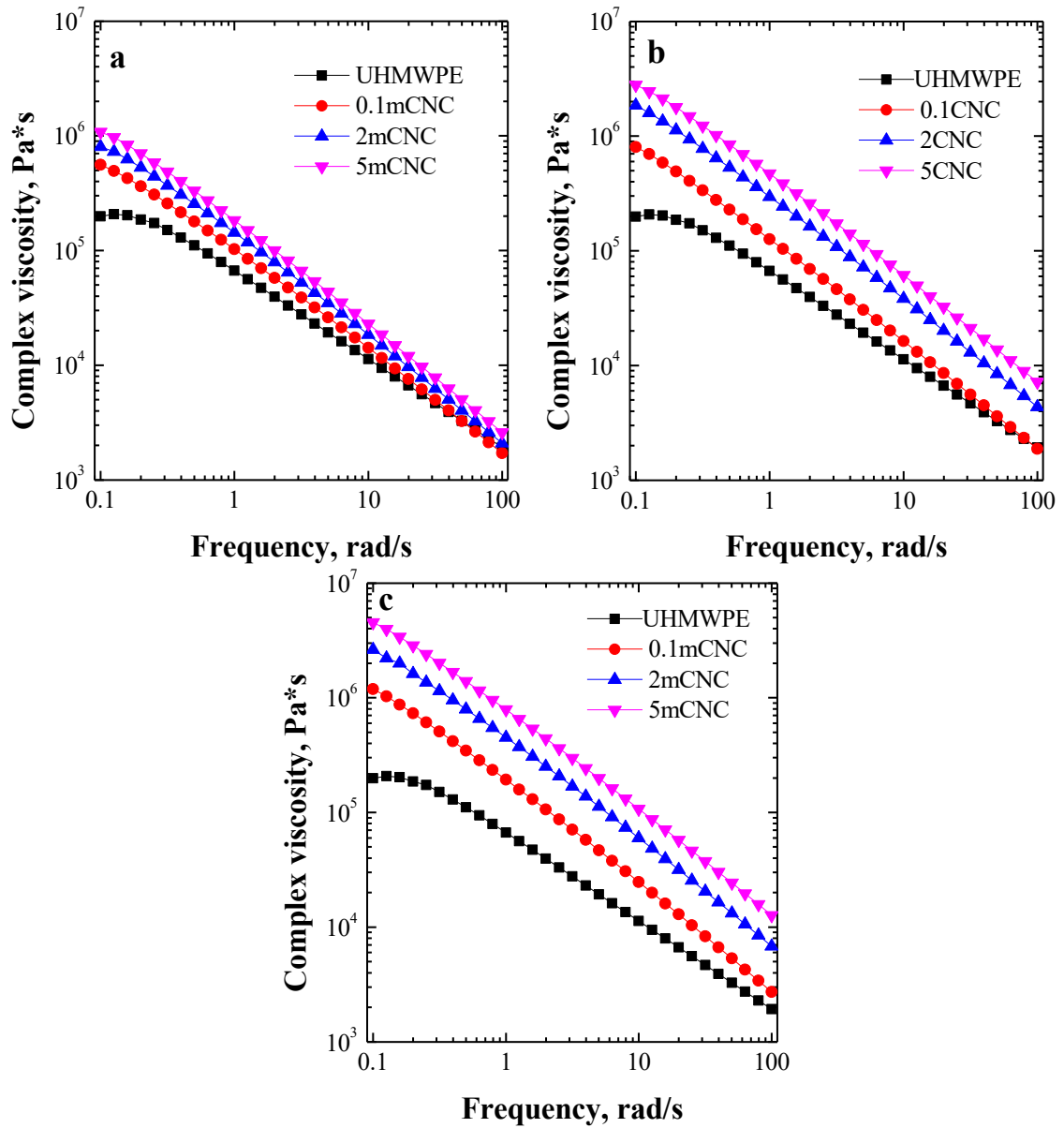
166 In Fig. 1, the complex viscosity as a function of frequency for all the investigated composites is reported  
167 and compared to that of unfilled matrix.

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.

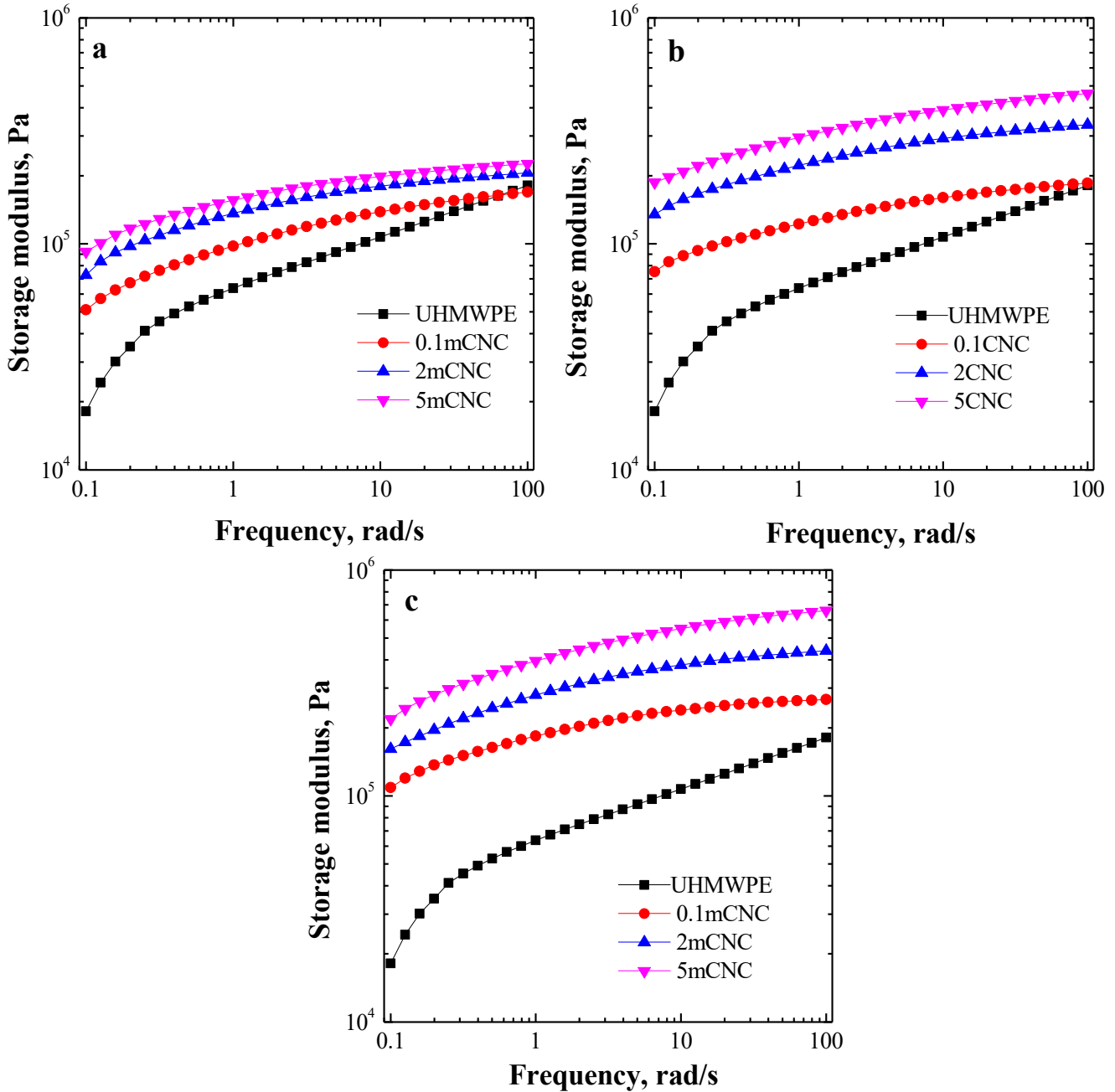


207

208

209

**Fig. 1** Complex viscosity as a function of frequency for (a) UHMWPE+mCNC<sub>dry</sub>, (b) UHMWPE+CNC<sub>wet</sub> and (c) UHMWPE+mCNC<sub>wet</sub> 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

210

211

212

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

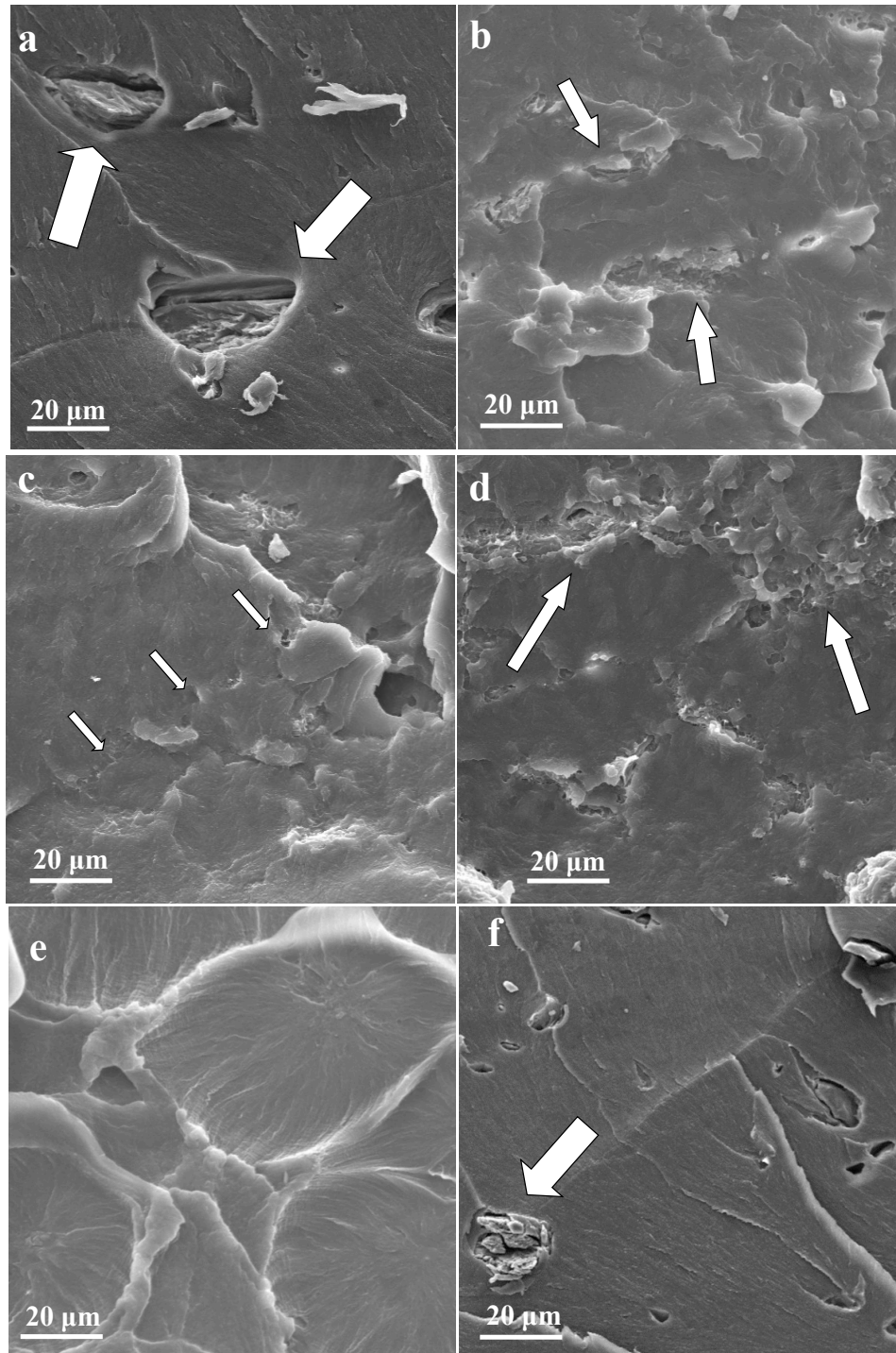
216 composites obtained through dry method, the embedded particles are uniformly dispersed within the host

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).

234



235

236

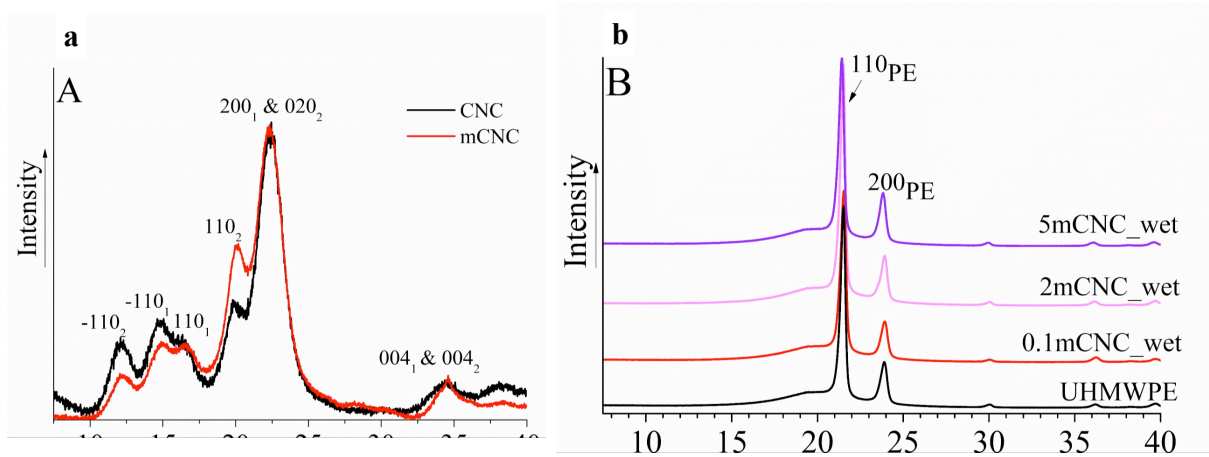
237

238

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. 200<sub>1</sub> &  
242 020<sub>2</sub> 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  $19.7^\circ$  are assigned to -110 and 110  
249 crystalline planes of cellulose II (Nishiyama et al. 2002). Peaks at  $2\theta = 14.7^\circ$  and  $16.5^\circ$  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 ( $\chi$ ) 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 200<sub>1</sub> & 020<sub>2</sub> peaks and 110<sub>2</sub>. 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).

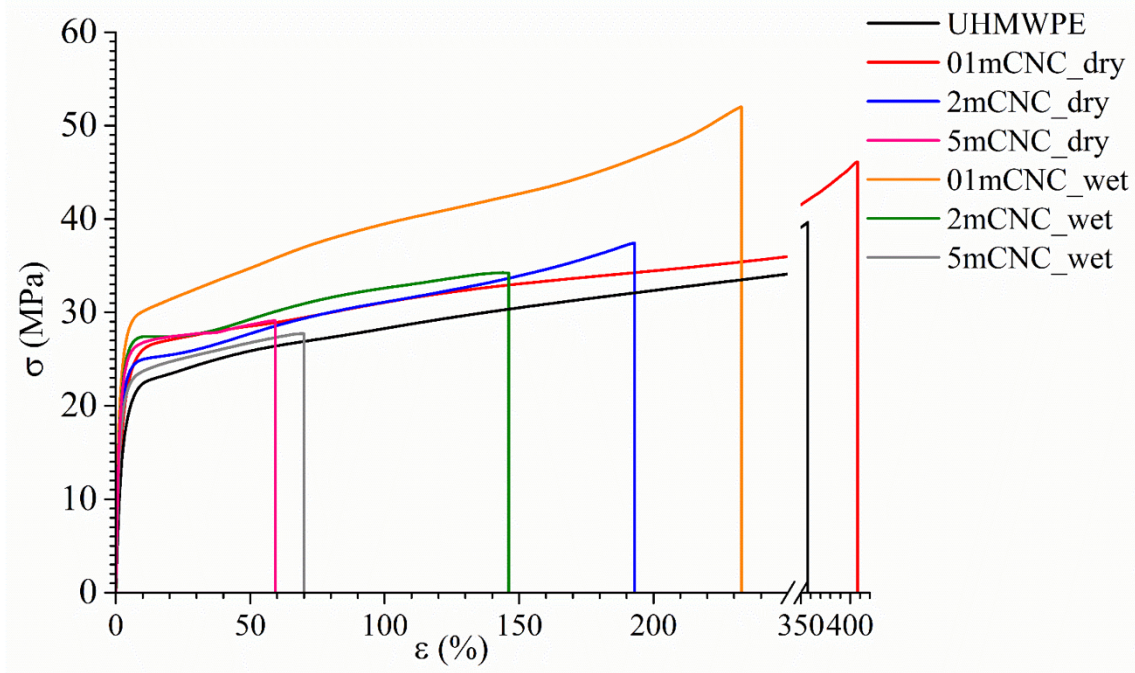
267 Fig. 4b reports the typical diffraction patterns of some UHMWPE/CNC composites. UHMWPE and all  
 268 the composites, regardless of the mixing technique, crystallize in the orthorhombic form of PE as  
 269 evidenced by the intense peaks at about  $2\theta = 21, 24$  and  $36^\circ$  corresponding 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 ( $\chi$  (WAXS)), Young modulus ( $E$ ), yield stress ( $\sigma_y$ ), stress ( $\sigma_b$ ) and strain ( $\epsilon_b$ ) at break of UHMWPE and its composites.

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

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

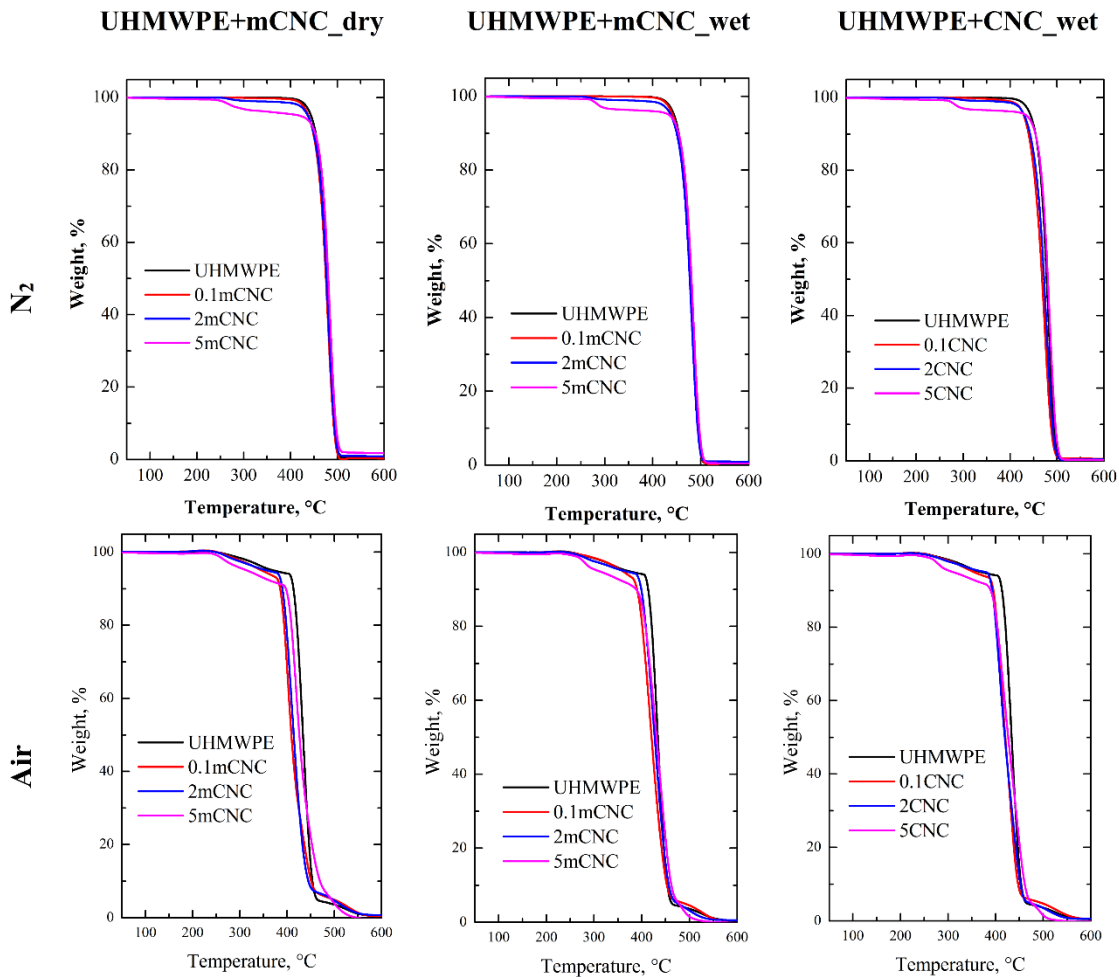
283 results found for other UHMWPE composites and can be ascribed to both their higher crystallinity degree  
284 with respect to that of unfilled polymer and to the reinforcement effect provided by the filler (Xie et al.  
285 2003; Suñer et al. 2015; Lombardo et al. 2016; Dorigato et al. 2013).  
286



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 N<sub>2</sub> 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 <sub>2</sub>				Atmosphere: air			
		T <sub>10%</sub> [°C]	T <sub>50%</sub> [°C]	T <sub>max</sub> [°C]	Residue @600°C [wt.%]	T <sub>10%</sub> [°C]	T <sub>50%</sub> [°C]	T <sub>max</sub> [°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

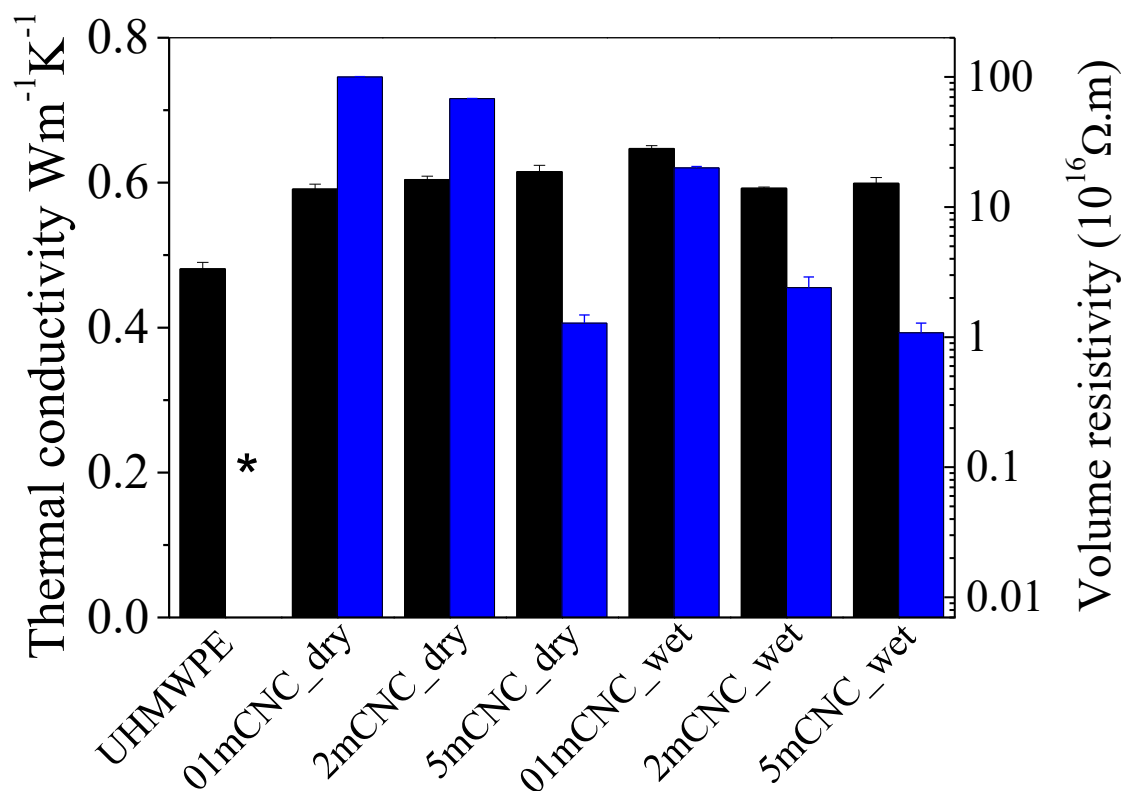
334

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  $9.99 \text{ W}$   
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

403 **Funding:** This research did not receive any specific grant from funding agencies in the public,  
404 commercial, or not-for-profit sectors.

405 **Conflicts of interest or competing interests:** The authors declare that they have no conflict of interest.

406 **Ethical approval:** This research does not contain any studies with human participants or animals  
407 performed by any of the authors.

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

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

410

411 **References**

- 412 Ago M, Endo T, Hirotsu T Crystalline transformation of native cellulose from cellulose I to cellulose II  
413 polymorph by a ball-milling method with a specific amount of water. Cellulose 11:163-167.  
414 doi:10.1023/B:CELL.0000025423.32330.fa
- 415 Blythe AR (1984) Electrical Resistivity Measurements of Polymer Materials. Polym Test 4:195-209.  
416 doi:10.1016/0142-9418(84)90012-6

417 Bras J, Viet D, Bruzzese C, Dufresne A (2011) Correlation between stiffness of sheets prepared from  
418 cellulose whiskers and nanoparticles dimensions. *Carbohydr Polym* 84:211-215.  
419 doi:10.1016/j.carbpol.2010.11.022

420 Bunn CW (1939) The crystal structure of long-chain normal paraffin hydrocarbons. The “shape” of the  
421 <CH<sub>2</sub> group. *Trans Faraday Soc* 35:482-491. doi:10.1039/TF9393500482

422 Chen Y, Qi Y, Tai Z, Yan X, Zhu F, Xue Q (2012) Preparation, mechanical properties and  
423 biocompatibility of graphene oxide/ultrahigh molecular weight polyethylene composites. *Europ Polym*  
424 *J* 48:1026-1033. doi:10.1016/j.eurpolymj.2012.03.011

425 Ching YC et al. (2016) Rheological properties of cellulose nanocrystal-embedded polymer composites:  
426 a review. *Cellulose* 23:1011–1030.

427 Dintcheva NT, Arrigo R, Carroccio S, Curcuruto G, Guenzi M, Gambarotti C, Filippone G (2016) Multi-  
428 functional Polyhedral Oligomeric Silsesquioxane-functionalized Carbon Nanotubes for photo-oxidative  
429 stable Ultra-High Molecular Weight Polyethylene-based Nanocomposites. *Europ Polym J* 75:525-537.  
430 doi:10.1016/j.eurpolymj.2016.01.002

431 Dorigato A, Pegoretti A, Dzenis Y (2013) Filler aggregation as a reinforcement mechanism in polymer  
432 nanocomposites. *Mech Mater* 61:79-90. doi:10.1016/j.mechmat.2013.02.004

433 Dufresne A (2012) *Nanocellulose: From Nature to High Performance Tailored Materials* Walter de  
434 Gruyter GmbH, Berlin/Boston

435 Duraccio D, Strongone V, Malucelli G, Auriemma F, De Rosa C, Mussano FD, Genova T, Faga MG  
436 (2019) The role of alumina-zirconia loading on the mechanical and biological properties of UHMWPE  
437 for biomedical applications. *Compos Part B Eng* 164:800-808. doi:10.1016/j.compositesb.2019.01.097

438 Duraccio D, Strongone V, Faga MG, Auriemma F, Mussano FD, Genova T, Malucelli G (2019) The role  
439 of different dry-mixing techniques on the mechanical and biological behavior of UHMWPE/alumina-  
440 zirconia composites for biomedical applications. *Europ Polym J* 120:109274.  
441 doi:10.1016/j.eurpolymj.2019.109274

442 Di Maro M, Duraccio D, Malucelli M, Faga MG (2021) High density polyethylene composites containing  
443 alumina-toughened zirconia particles: Mechanical and tribological behavior. *Composites Part B:*  
444 *Engineering* 217:108892. doi.org/10.1016/j.compositesb.2021.108892

445 Favier V, Canova GR, Cavallè JY, Chanzy H, Dufresne A, Gauthier C (1995) Nanocomposite materials  
446 from latex and cellulose whiskers. *Polym Adv Technol* 6:351–355. doi:10.1002/pat.1995.220060514

447 Feng CP, Chen L, Wei F, Ni NY, Chen J, Yang W (2016) Highly thermally conductive  
448 UHMWPE/graphite composites with segregated structures. *RSC Adv* 6:65709-65713.  
449 doi:10.1039/C6RA13921C

450 French AD, Santiago CM (2013) Cellulose polymorphy, crystallite size, and the Segal crystallinity.  
451 *Cellulose* 20:583-588. doi:10.1007/s10570-012-9833-y

452 Garvey CJ, Parker IH, Simon GP (2005) On the interpretation of X-ray diffraction powder patterns in  
453 terms of the nanostructure of cellulose I fibers. *Macromol Chem Phys* 206:1568-1575.  
454 doi:10.1002/macp.200500008

455 Gu J, Guo Y, Lv Z, Geng W, Zhang Q (2015) Highly thermally conductive POSS-g-SiCp/UHMWPE  
456 composites with excellent dielectric properties and thermal stabilities. *Compos Part A Appl. Sci* 78:95-  
457 101. doi:10.1016/j.compositesa.2015.08.004

458 Gu J, Li N, Tian L, Lv Z, Zhang Q (2015) High thermal conductivity graphite nanoplatelet/UHMWPE  
459 nanocomposites. *RSC Adv* 5:36334–36339. doi:10.1039/C5RA03284A

460 Guo Y, Cao C, Luo F, Huang B, Xiao L, Qian Q, Chen Q (2019) Largely enhanced thermal conductivity  
461 and thermal stability of ultra high molecular weight polyethylene composites via BN/CNT synergy. *RSC*  
462 *Adv* 9:40800-40809. doi:10.1039/C9RA08416A

463 Gustavsson M, Karawacki E, Gustafsson SE (1994) Thermal conductivity, thermal diffusivity, and  
464 specific heat of thin samples from transient measurements with hot disk sensors. *Rev Sci Instrum*  
465 65:3856-3859. doi:10.1063/1.1145178

466 Gürgen S (2019) Wear performance of UHMWPE based composites including nano-sized fumed silica.  
467 *Compos Part B Eng* 173:106967. doi:10.1016/j.compositesb.2019.106967

468 Hamed MM, Hajian A, Fall AB, Hakansson K, Salajkova M, Lundell F, Wagberg L, Berglund LA  
469 (2014) Highly Conducting, Strong Nanocomposites Based on Nanocellulose-Assisted Aqueous  
470 Dispersions of Single-Wall Carbon Nanotubes. *ACS Nano* 8:2467-2476. doi:10.1021/nn4060368

471 Hussain M, Naqvi RA, Abbas N, Khan SM, Nawaz S, Hussain A, Zahra N, Khalid MW (2020) Ultra-  
472 High-Molecular-Weight-Polyethylene [UHMWPE] as a Promising Polymer Material for Biomedical  
473 Applications: A Concise Review. *Polymers* 12:323. doi:10.3390/polym12020323

474 Kargarzadeh H, Ahmad I, Abdullah I, Dufresne A, Zainudin SY, Sheltami RM (2012) Effects of  
475 hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals  
476 extracted from kenaf bast fibers. *Cellulose* 19:855-866. doi:10.1007/s10570-012-9684-6

477 Khumalo VM., Karger-Kocsis J, Thomann R (2011) Polyethylene/synthetic boehmite alumina  
478 nanocomposites: structure, mechanical, and perforation impact properties. *J. Mater. Sci.* 46:422–428.  
479 doi.org/10.1007/s10853-010-4882-9

480 Lombardo G, Bracco P, Thornhill TS, Bellare A (2016) Crystallization pathways to alter the nanostructure  
481 and tensile properties of non-irradiated and irradiated, vitamin E stabilized UHMWPE. *Europ Polym J*  
482 75:354-362. doi:10.1016/j.eurpolymj.2015.12.028

483 Mariano M, El Kissi N, Dufresne A (2014) Cellulose nanocrystals and related nanocomposites: Review  
484 of some properties and challenges. *J Polym Sci Part B Polym Phys* 52:791-806. doi:10.1002/polb.23490

485 Martínez-Morlanes MJ, Castell P, Martínez-Nogués V, Martínez MT, Alonso PJ, Puértolas JA (2011)  
486 Effects of gamma-irradiation on UHMWPE/MWNT nanocomposites. *Compos Sci Technol* 71:282-288.  
487 doi:10.1016/j.compscitech.2010.11.013

488 Michler GH, Kausch-Blecken von Schmelting HH. 2013 The physics and micro-mechanics of nano-voids  
489 and nano-particles in polymer combinations. *Polym.* 54:3131-3144.  
490 doi.org/10.1016/j.polymer.2013.03.035

491 Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose  
492 Ib from synchrotron X-ray and neutron fiber diffraction. *J Am Chem Soc* 124:9074-9082.  
493 doi:10.1021/ja0257319

494 Pang W, Ni Z, Chen G, Huang G, Huang H, Zhao Y (2015) Mechanical and thermal properties of  
495 graphene oxide/ultrahigh molecular weight polyethylene nanocomposites. *RSC Adv* 5:63063-63072.  
496 doi:10.1039/C5RA11826C

497 Plumlee K, Schwartz CJ (2009) Improved wear resistance of orthopaedic UHMWPE by reinforcement  
498 with zirconium particles. *Wear* 267:710-717. doi:10.1016/j.wear.2008.11.028

499 Reddy SK, Kumar S, Varadarajan KM, Marpu PR, Gupta TK, Choosri M (2018) Strain and damage-  
500 sensing performance of biocompatible smart CNT/UHMWPE nanocomposites. *Mater Sci Eng C* 92:957-  
501 968. doi:10.1016/j.msec.2018.07.029

502 Ren PG, Hou SY, Ren F, Zhang ZP, Sun ZF, Xu L (2016) The influence of compression molding  
503 techniques on thermal conductivity of UHMWPE/BN and UHMWPE/[BN+MWCNT] hybrid  
504 composites with segregated structure. *Compos Part A Appl Sci* 90:13-21.  
505 doi:10.1016/j.compositesa.2016.06.019

506 Rietveld HM (1967) Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta*  
507 *Crystallogr* 22:151-152. doi:10.1107/S0365110X67000234

508 Rodrigues MM, Fontoura CP, Maddalozzo AED, Leidens LM, Quevedo HG, dos Santos Souza K, da  
509 Silva Crespo J, Fassini Michels A, Figueroa CA, Aguzzoli C (2020) Ti, Zr and Ta coated UHMWPE  
510 aiming surface improvement for biomedical purposes. *Compos Part B Eng* 189:107909.  
511 doi:10.1016/j.compositesb.2020.107909

512 Roman M, Winter WT (2004) Effect of Sulphate Groups from Sulfuric Acid Hydrolysis on the Thermal  
513 Degradation Behavior of Bacterial Cellulose. *Biomacromolecules* 5:1671-1677.  
514 doi:10.1021/bm034519+

515 Ruan S, Gao P, Yu TX (2006) Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled  
516 carbon nanotubes. *Polymer* 47:1604-1611. doi:10.1016/j.polymer.2006.01.020

517 Russo P, Patti A, Petrarca C, Acierno S (2018) Thermal conductivity and dielectric properties of  
518 polypropylene-based hybrid compounds containing multiwalled carbon nanotubes. *J Appl Polym Sci*  
519 135:46470. doi:10.1002/app.46470

520 Sattari M, Naimi-Jamal MR, Khavandi A (2014) Interphase evaluation and nano-mechanical responses  
521 of UHMWPE/SCF/nano-SiO<sub>2</sub> hybrid composites. *Polym Test* 38:26–34.  
522 doi:10.1016/j.polymertesting.2014.06.006

523 Schwanninger M, Rodrigues JC, Pereira H, Hinterstoisser B (2004) Effects of short-time vibratory ball  
524 milling on the shape of FT-IR spectra of wood and cellulose. *Vib Spectrosc* 36:23-40.  
525 doi:10.1016/j.vibspec.2004.02.003

526 Segal L, Creely JJ, Martin AE, Conrad CM (1959) An empirical method for estimating the degree of  
527 crystallinity of native cellulose using the X-ray diffractometer. *Text Res J* 29:786-794.  
528 doi:10.1177/004051755902901003

529 Shanmugam L, Feng X, Yang J (2019) Enhanced interphase between thermoplastic matrix and  
530 UHMWPE fiber sized with CNT-modified polydopamine coating. *Compos Sci Technol* 174:212-220.  
531 doi:10.1016/j.compscitech.2019.03.001

532 Shojaeiarani J et al. (2021) Cellulose nanocrystal based composites: A review. *Composites Part C: Open*  
533 *Access* 5:100164.

534 Suñer S, Joffe R, Tipper JL, Emami N (2015) Ultra high molecular weight polyethylene/graphene oxide  
535 nanocomposites: Thermal, mechanical and wettability characterisation. *Compos Part B Eng* 78:185-191.  
536 doi:10.1016/j.compositesb.2015.03.075

537 Thygesen A, Oddershede J, Lilholt H, Thomsen AB, Ståhl K (2005) On the determination of crystallinity  
538 and cellulose content in plant fibre. *Cellulose* 12:563-576. doi:10.1007/s10570-005-9001-8.

539 Wang S, Feng Q, Sun J, Gao F, Fan W, Zhang Z, Li X, Jiang X (2016) Nanocrystalline Cellulose  
540 Improves the Biocompatibility and Reduces the Wear Debris of Ultrahigh Molecular Weight  
541 Polyethylene via Weak Binding. *ACS Nano* 10:298-306. doi:10.1021/acsnano.5b04393

542 Wang X, Lu H, Feng C, Ni H, Chen J (2020) Facile method to fabricate highly thermally conductive  
543 UHMWPE/BN composites with the segregated structure for thermal management. *Plastics, Rubber and*  
544 *Composites* 49:196-203. doi:10.1080/14658011.2020.1726143

545 Wang Y, Qiao X, Wan J, Xiao Y, Fan X (2016) Preparation of AlN microspheres/UHMWPE composites  
546 for insulating thermal conductors. *RSC Adv* 6:80262-80267. doi:10.1039/C6RA18228C

547 Wang ZG, Gong F, Yu WC, Huang YF, Zhu L, Lei J, Xu JZ, Li ZM (2018) Synergetic enhancement of  
548 thermal conductivity by constructing hybrid conductive network in the segregated polymer composites.  
549 *Compos Sci Technol* 162:7-13. doi:10.1016/j.compscitech.2018.03.016

550 Wu X, Liu W, Ren L, Zhang C (2020) Highly thermally conductive boron nitride@UHMWPE  
551 composites with segregated structure. *e-Polymers* 20:510-518. doi.org/10.1515/epoly-2020-0053

552 Xie XL, Tang CY, Chan KYY, Wu XC, Tsui CP, Cheung CY (2003) Wear performance of ultrahigh  
553 molecular weight polyethylene/quartz composites. *Biomaterials* 24:1889-1896. doi:10.1016/S0142-  
554 9612(02)00610-5

555 Xue Y, Wu W, Jacobs O, Schadel B (2006) Tribological behaviour of UHMWPE/HDPE blends  
556 reinforced with multi-wall carbon nanotubes. *Polym Test* 25:221-229.  
557 doi:10.1016/j.polymertesting.2005.10.005

558 Zhang Z, Wu QL, Song KL, Ren SX, Lei TZ, Zhang QG (2015) Using Cellulose Nanocrystals as a  
559 Sustainable Additive to Enhance Hydrophilicity, Mechanical and Thermal Properties of Poly[Vinylidene  
560 Fluoride]/Poly[Methyl Methacrylate] Blend. *ACS Sust Chem Eng* 3:574-582. doi:10.1021/sc500792c

561 Zhou W, Chen Q, Sui X, Dong L, Wang Z (2015) Enhanced thermal conductivity and dielectric properties  
562 of Al/ $\beta$ -SiC w/PVDF composites. *Compos Part A Appl Sci* 71:184-191.  
563 doi:10.1016/j.compositesa.2015.01.024

564 Zhou W, Qi S, Li H, Shao S (2007) Study on insulating thermal conductive BN/HDPE composites.  
565 *Thermochim Acta* 452:36-42. doi:10.1016/j.tca.2006.10.018

566 Zhou Y, Liu F, Wang H (2017) Novel organic-inorganic composites with high thermal conductivity for  
567 electronic packaging applications: A key issue review. *Polym Compos* 38:803-813. doi:10.1002/pc.2364

568 Zhou Y, Wang H, Wang L, Yu K, Lin Z, He L, Bai Y (2012) Fabrication and characterization of  
569 aluminum nitride polymer matrix composites with high thermal conductivity and low dielectric constant  
570 for electronic packaging. *Mater Sci Eng B* 177:892-896. doi: 10.1016/j.mseb.2012.03.056