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1 Article

2 Key Role of the Dispersion of carbon nanotubes (CNTs) 3 within Epoxy Networks on their ability to Release

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6

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12

13 **Abstract:** Carbon nanotubes (CNT) reinforced nanocomposites represent an unique opportunity in
14 terms of designing advanced materials with mechanical reinforcement and electrical and thermal
15 conductivities improvements. However, toxic effects of these composites on human health still have
16 been studied and very soonly some regulations on CNT and on composites based on CNT will be
17 enacted. That is why CNT releasing during nanocomposites lifecycle must be controlled. As the
18 releasing depends on the interfacial strength that is stronger between CNT and polymer compared
19 to CNTs in a CNTs agglomerate, two dispersion states, one poorly dispersed *versus* another well
20 dispersed are generated and finely described. So the main aim of this study is to check if CNT
21 dispersion state has an influence on the CNT potential releasing in the nanocomposite. To well tailor
22 and characterize the CNT dispersion state in the polymer matrix, the electronic microscopies (SEM
23 and TEM) but also the rheological analysis are carried out to well identify if CNTs are isolated, in
24 bundles or in agglomerates. When the dispersion state is known and controlled, its influence on the
25 polymerization kinetic and on mechanical properties is discussed. It appears clearly that in the case
26 of good dispersion state, strong interfaces are generated linking the isolated nanotubes with the
27 polymer whereas the CNT cohesion in an agglomerate seems much more weak and it does not
28 provide any improvement to the polymer matrix. Raman spectroscopy is relevant to analyze the
29 interfacial properties and allows the relationship with the releasing ability of nanocomposites, *i.e.*
30 CNTs poorly dispersed in the matrix are more readily released when compared to well dispersed
31 nanocomposites. The tribological tests confirm from released particles granulometry and
32 observations that a CNT dispersion state sufficiently achieved in the nanocomposite avoids single
33 CNT releasing under those solicitations.

34

35 **Keywords:** Carbon nanotube, epoxy networks, releasing

36

37

38 1. Introduction

39 Carbon nanotubes (CNTs) always have been very attractive nanofillers because of their remarkable
40 properties. CNTs exhibit an extraordinary large specific surface area depending on diameter
41 combined to an exceptionally high stiffness and electrical conductivity [1]. As a result, CNTs have a
42 real potential for processing the polymer composites and for getting mechanical reinforcement but
43 also thermal and electrical conductivities improvement while making the materials more lightweight
44 [2-4]. However the toxicological effects of CNTs on human health are still under study regarding
45 morphological similarities with asbestos and other small fibers [5-6-7]. A release of nanotubes can
46 occur not only during the CNTs production but also during the use of manufactured nanocomposites
47 [8]. Tailoring the releasing of isolated CNT during the nanocomposites lifecycle and especially during
48 the different steps of handling (like friction, mechanical abrasion or breakage) is strongly required
49 for a responsible development of these NTC nanofilled polymers materials [9-10]. Up to now, the risk
50 caused by the exposure to CNTs has been hard to evaluate by lacking of data about the impacts on
51 human health and the environment. Precautionary measures have been recommended to protect the
52 workers, users and the environment. The potential release of CNTs from composite materials as a
53 result of cutting, drilling, sanding, grinding and UV-light weathering has been investigated [11]. Most
54 of them reported the particles generated were predominantly micron sized with protruding CNTs
55 but generally without isolated NTCs [12-14]. Only Schlagenhauf *et al* showed the release of free-
56 standing individual CNTs from CNTs-embedded nanocomposites in addition of abraded particles
57 from the epoxy matrix and agglomerates of CNTs during an abrasion process [15]. Nanocomposites
58 are processed by a wide variety of mixing protocols and include a range of formulations that can
59 impact how CNTs are integrated and encapsulated within the composite. Kohler *et al* showed that
60 the likelihood and form of release of nanotubes were determined by the way CNTs are incorporated
61 into the material [16]. In order to understand the toxicological potential of handling CNT-containing
62 composites, characterizing and quantifying the amount of free CNTs versus matrix-bound ones is
63 relevant. A good dispersion state of the nanotubes in the matrix is required to increase the composite
64 performances but what about the impact of this dispersion state on the CNT releasing process in the
65 environment ? Interactions between a CNT and the surrounding polymer matrix and between CNTs
66 in nanotubes agglomerates are significantly different. Several literature works review the different
67 methods to evaluate and measure the interfacial stress, *i.e.* IFSS, between a CNT and a polymer matrix
68 and between two CNTs. Even if very different values of IFSS are reported depending on the type of
69 measurement approach, computational simulations versus experimental microdebonding tests, these
70 ones are high are due to strong physical and chemical bonds at the CNT/polymer interface [17-21].
71 An average value of 100 MPa can be kept in mind against only 1 MPa for the interfacial stresses
72 existing between two CNTs side by side (such as encountered in CNT agglomerates) which
73 corresponds to the stress necessary to overcome Van der Waals interactions [22-24]. As a result, this
74 study consisted in i) generating different dispersion states of CNT within an epoxy matrix from
75 masterbatch in order to get either individually dispersed CNT or CNT agglomerates and ii) finely
76 characterizing those dispersion states thanks to different multiscale approaches in order to well
77 understand the impact of the nanocomposite morphology on its ability to release particules during
78 its lifetime.

79 2. Materials and Methods

80 2.1-Materials

81

82 The epoxy prepolymer is the diglycidyl ether of Bisphenol A LY556 from Huntsman Co. (DGEBA,
83 $\bar{n} = 0.15$). The hardener chosen the diaminodiphenylsulfone denoted as DDS from Aldrich is added
84 with a stoichiometric ratio aminohydrogen to epoxy equal to 1. This hardener leads to a network with
85 a high Tg equal to 220°C after curing 2 hours at 150°C and 3 hours at 220°C. The CNT used in this
86 study are multiwall carbon nanotubes, MWNT, provided by Arkema under the form of a DGEBA-
87 based masterbatch (25 wt% MWNT). The CNTs have a mean outer diameter of 12 nm and a mean
88 inner diameter of 5 nm. Their length is from 100 nm to several μm (average length of about 800 nm).

89

90 2.2-Nanocomposite processing

91

92 In order to get the proper weight fraction of CNT in the nanocomposite, the masterbatch is diluted in
93 the DGEBA prepolymer to get 1 wt% in the DGEBA prepolymer leading to 0.7 wt% of CNT in the
94 final nanocomposite. Different processing conditions have been applied to generate varying
95 dispersion states, *i.e.* from large MWNT agglomerates, as in the masterbatch before dispersion, to
96 nearly individually dispersed nanotubes. Two tools with different shearing rates have been
97 compared : i) a rotary blade Turbotest Rayneri (with a speed of rotation set at 2000 rpm) and ii) a 3
98 roll-mill Exakt 80E.

99

100 2.3-Characterization of the dispersion state

101

102 2.3.1. In DGEBA prepolymer-CNT suspensions

103

104 Investigating the rheological properties of nanofilled suspensions is known to be a powerful method
105 to understand the nanofillers organization into a liquid medium such as DGEBA prepolymer.
106 Frequency sweep tests were performed from 100 to 0.1 rad/s using an AR1000 (TA) rheometer with
107 a cone-plate geometry in the linear viscoelastic region of DGEBA/MWNT suspensions.

108

109 2.3.2. In nanocomposites at the solid state

110

111 The morphology of nanocomposites, *i.e.* cured systems, is observed by Scanning Electronic
112 Microscopy (SEM) using a Philips XL 20 microscope and by Transmission Electronic Microscopy
113 (TEM) using a 1200EX Jeol microscope. Specimens for TEM observations have been prepared using
114 ultramicrotomy at room temperature.

115

116 2.4-Cure kinetics

117

118 2.4.1. Epoxy conversion rate and activation energy of reaction

119

120 In order to determine if CNTs have an influence on the epoxy conversion rate during the
121 polymerization of epoxy-amine reactive systems, cure kinetics were carried out during 2 hours at
122 150°C (first step of the curing cycle). The extent of reaction for given times was calculated from the
123 exothermal peak of residual reaction of polycondensation, ΔHr (J/g), compared to the total heat of
124 reaction, ΔHt (J/g). According to the Kissinger method, the activation energy of the condensation
125 reaction can be deduced from differential scanning calorimetry experiments, DSC, at different
126 heating rates, *i.e.* 2.5, 5, 10 and 15 K.min⁻¹, from 30 to 350°C in order to get a complete reaction.
127 Calorimetric measurements have been performed on the Q20 calorimeter from TA Instruments.

128

129 2.4.2. Gelation time determination

130

131 Multifrequency time sweep tests were performed on ARES with a plate/plate geometry to determine
132 gel times of the epoxy/amine systems with or without CNT from the isofrequency crossover point of
133 the $\tan \delta$ curves during an isothermal curing (at 150°C).

134

135 2.5-Nanocomposite characterization

136

137 2.5.1. Mechanical behavior

138

139 Flexural modulus, stress at break and toughness of nanocomposites were measured and discussed as
140 a function of dispersion states. The flexural properties have been measured at 25°C on a 2/M device
141 from MTS. Flexural Young's modulus and stress at break have been determined considering three
142 points bending tests on machined samples (75 x 15 x 3 mm³). The fracture toughness has been
143 evaluated at 25°C in order to determine critical stress intensity factor K_{Ic} on single edge notched
144 samples (SEN) in three points bending mode.

145

146 2.5.2. Microscopy and Raman spectroscopy to analyze the stress transfer

147

148 Nanocomposites samples were fractured into liquid nitrogen for SEM (Scanning Electronic
149 Microscopy) fracture analysis (Philips XL 20). Plastic deformation at crack tip was also analysed using
150 TEM (Transmission Electronic Microscopy) on a 1200EX Jeol.

151 Micro-Raman measurements were realized on the nanocomposites having different dispersion states
152 under compression. The spectra for the CNT were recorded using a Jobin Yvon Raman system
153 operating at 514 nm.

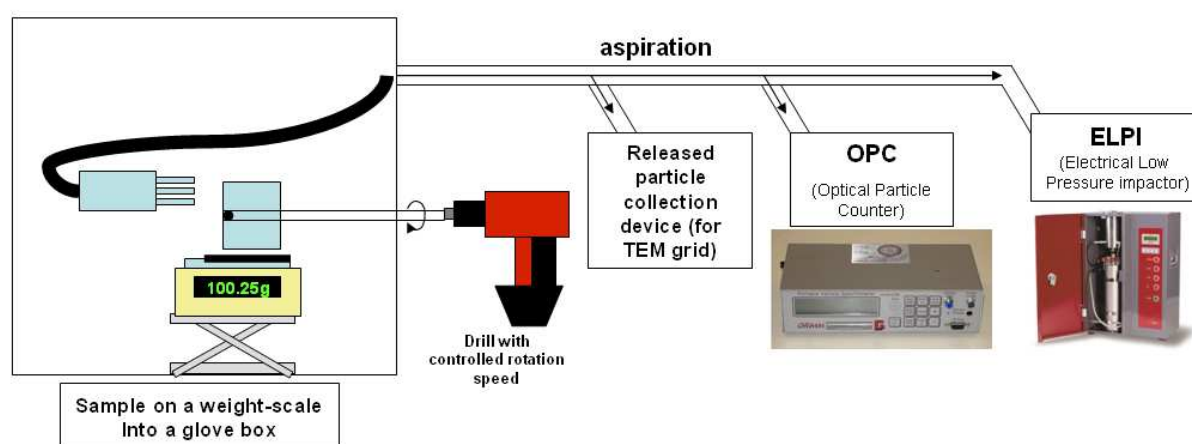
154

155 2.6- Characterization of particles release

156

157 A tribological process represented in Figure 1 and already described in a previous paper was
158 developed in order to analyze airborne particles which were released by the nanocomposite under
159 mechanical wear [13]. The nanomaterial is disposed in a clean glove box using a light air flow filtered
160 with an H14 HEPA filter leading to a very low background level of nanoparticles (5–10 cm⁻³). In order
161 to simulate two different mechanical wear, a circular brush in steel is used to simulate abrasion and

162 a steel rake to simulate scratching. The normal force applied on the sample by the tool is controlled
 163 thanks to an analytical balance. A load of 50 g is applied on each sample with a speed of 1500 rotation
 164 per minute during 30 seconds of solicitation followed by 30 seconds of “rest”. The ‘airborne particles
 165 characterization part is composed of a particles collection device on a TEM grid (VTT filtration
 166 device), an OPC (optical particle counter) Grimm 1.109 which is spectrometer giving airborne
 167 particles granulometric measurement from 250 nm to 35 μm (optical diameter) and an ELPI (electrical
 168 low pressure impactor) which gives the airborne particles granulometric measurement from 7 nm to
 169 10 μm (aerodynamic diameter). In this work only the ELPI granulometric results will be presented
 170 since the OPC granulometric results were not sensitive enough to provide information at the
 171 nanometric scale (lower limit at 250 nm is not appropriate to detect isolated CNT).



172
 173 **Figure 1.** Representation of the wear simulation device in order to analyze airborne released particles

174 175 3-Results and discussion

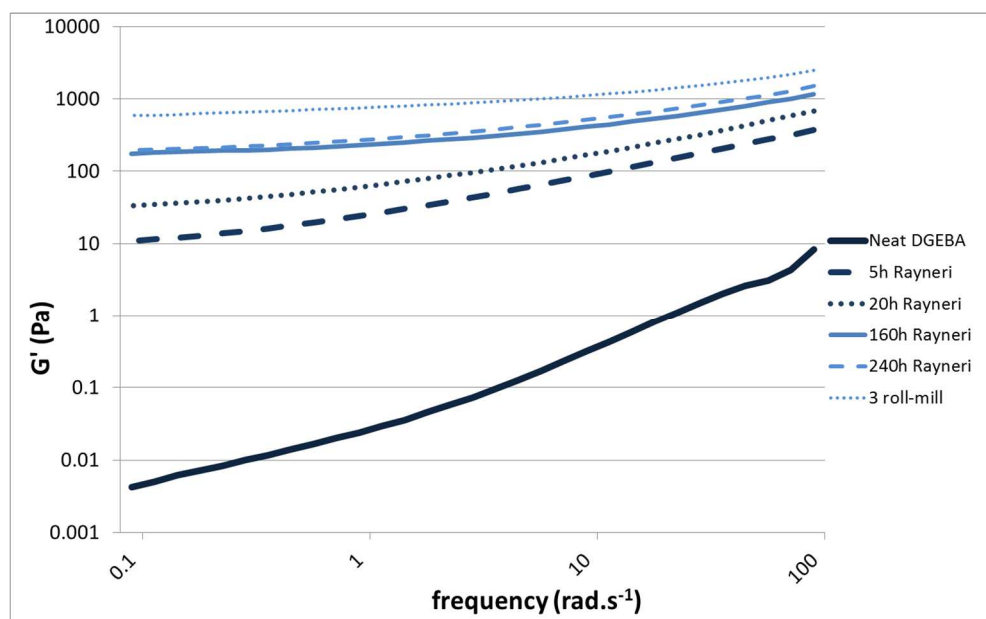
176 177 3.1-Structuration of carbon nanotubes

178
 179 Generating different dispersion states of CNT in a controlled way remains challenging. Tuning the
 180 processing parameters was the chosen pathway to generate extreme morphologies, *i.e.* aggregated vs
 181 dispersed. The organization of CNT within the epoxy material was studied : i) before curing, *i.e.* as
 182 the CNT-based masterbatch is dispersed in the DGEBA prepolymer and ii) after curing, *i.e.* in the
 183 solid state nanocomposites.

184 185 3.1.1. Structuration of CNT in the DGEBA-CNT suspensions

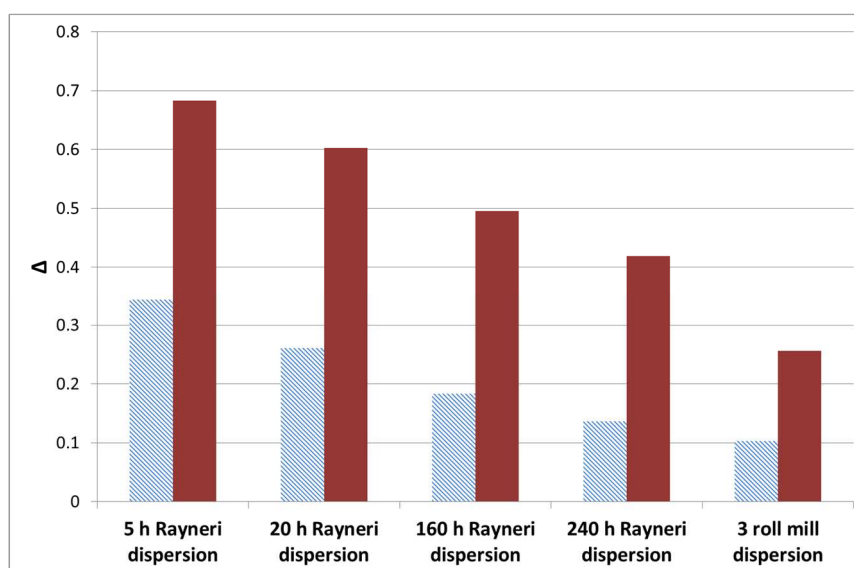
186
 187 The rheology of suspensions is very sensitive to the CNT dispersion state (individually dispersed *vs*
 188 aggregated) [25-27]. In the case of a very good dispersion, the formation of a percolated network can
 189 be highlighted from the appearance of a plateau for storage modulus G' at low frequencies in the
 190 linear domain which is a signature of an elastic response at a given volume fraction. The changes in

191 the G' dependence with frequency in the low frequencies region, *i.e.* the exponent of the power law
 192 $f(\omega)$ decreases from 2 (liquid-like) to 0 (gel-like), could be the way to determine clearly the percolation
 193 threshold for different volume fractions of CNT. Thus, the rheological signatures of different
 194 suspensions (prepared with the same CNT weight percentage) can be compared in terms of
 195 dispersion state [25-27]. Different dispersion states of 1 wt% CNT in DGEBA prepolymer while
 196 varying dispersion tools were studied from 100 to 0.1 rad/s in dynamic mode (Figure 2). As expected
 197 the increase of the mixing time combined with the use of a high shear tool enhances the dispersion
 198 efficiency in the prepolymer. The rheological behavior of the initial DGEBA prepolymer displays a
 199 Newtonian behavior (storage modulus G' proportional to ω^2) whereas a solid-like behavior is
 200 evidenced as the prepolymer is filled with 1 wt% of CNT, *i.e.* G' becomes independent on the
 201 frequency at low frequencies. This evolution of G' at low frequencies is more pronounced as the 3
 202 roll-mill calander is used. The storage modulus values at the lowest frequency, *i.e.* at 0.1 rad/s, as well
 203 as its dependence at low frequencies according to the power law, $G' \sim \omega^\Delta$, are reported in Figures 2
 204 and 3 as a function of the dispersion conditions. The same conclusions can be made from loss
 205 modulus (G'') dependence in frequency.



206
 207
 208
 209

Figure 2. Evolution of storage modulus (G') as a function of frequency, 0.1 % of dynamic strain at 25°C, for DGEBA/MWNT suspensions (1 wt%) with different mixing conditions



210
211

212 **Figure 3.** Δ exponent from the power law of G' (hatched light) and G'' (full dark) with the frequency (from 0.1
213 to 1 rad/s) at 25°C for DGEBA/MWNT suspensions (1 wt%) with different mixing conditions
214

215 Adding 1 % by weight of MWNT leads to a very pronounced effect on the rheological behavior of the
216 suspension but it strongly depends on the dispersion state. The rheological signature of the
217 suspension after 5 hours of Rayneri dispersion is completely different from the one with the best
218 dispersion state, *i.e.* obtained using the 3 roll-mill, as G' increases by almost 2 orders of magnitude
219 and the exponent of the G' dependence with frequency is almost divided by 4. Hence, the dispersion
220 state of CNT suspension in DGEBA prepolymer, for a given content of CNT, could be quantified
221 using rheological parameter such as dependence of storage modulus versus frequency in terminal
222 region [28].

223

224 3.1.2. Dispersion state characterization in the final nanocomposite

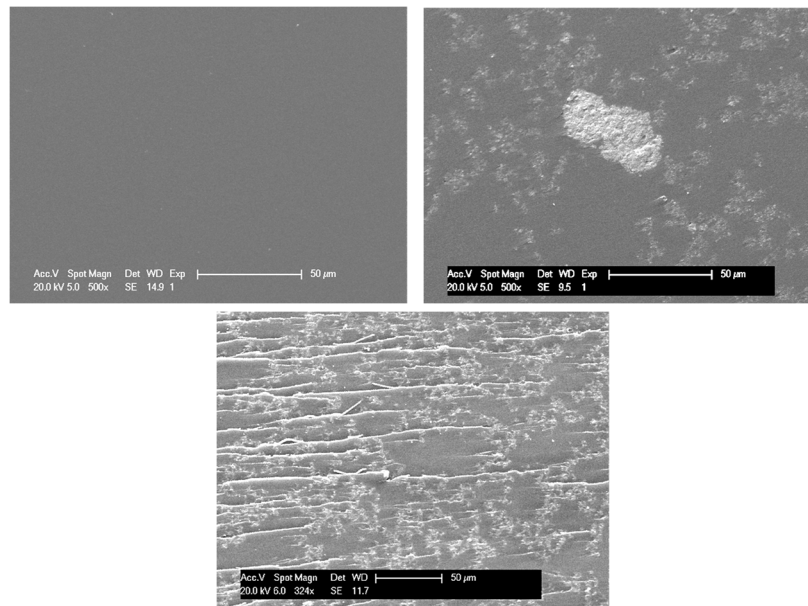
225

226 The final morphology at the solid state of nanocomposites results from the freezing of the dispersion
227 state existing on uncured DGEBA/MWNT dispersion and potential changes of the dispersion state
228 during the 3D growing of the epoxy network during cure. Actually, the polymerization process may
229 stabilize the dispersion state obtained before adding the amine hardener or in the opposite may
230 modify the morphology. In order to analyze the CNT dispersion into the thermoset matrix, several
231 methods could be used such as electron microscopies SEM and TEM which could allow to get precise
232 information like aggregate size distributions, interparticles distances etc. For the nanocomposites
233 having the poorest dispersion state, SEM microscopy reveals the presence of aggregates and even of
234 agglomerates which have mean sizes around a few tens of micrometers (

235 Figure 4-right). The comparison between nanocomposites having different states of dispersion (
236 Figure 4) shows clearly the efficiency of the 3 roll-mill calander to avoid micron-size agglomerates
237 that are observed after a dispersion of 5 hours with Rayneri rotary blade which is much less effective.
238

238

239

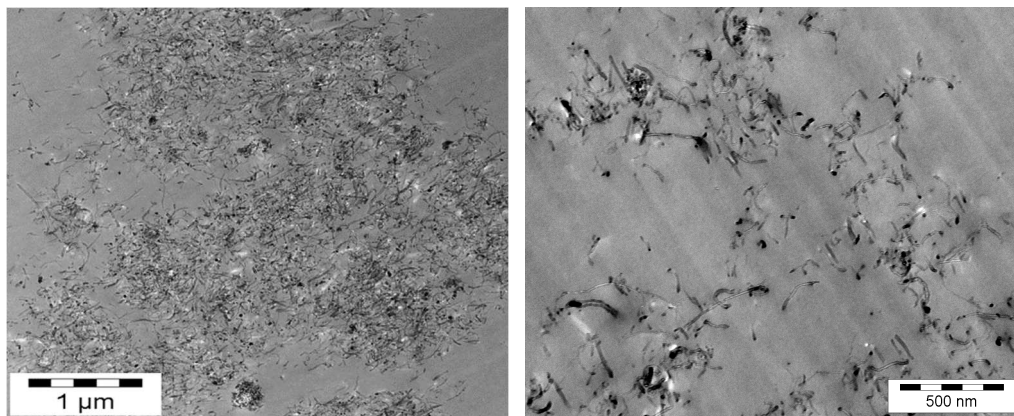
240
241

242 **Figure 4.** SEM micrograph of unfilled epoxy network (left), epoxy/DDS/MWNT nanocomposite (0.7 wt%) after
 243 a 5 h dispersion with Rayneri (right) and epoxy/DDS/MWNT nanocomposite (0.7 wt%) after a dispersion with
 244 3 roll-mill calander (below)

245

246 As reported in a previous paper dedicated to nanoclay-based nanocomposite morphologies, the
 247 dispersion needs to be defined at different scales : from large micrometer size aggregates or
 248 agglomerates to nanoscale which is the scale of the individual nanofillers [29]. TEM (Transmission
 249 Electronic Microscopy) is a powerful method to achieve nanometric scale characterizations.

250



251

252 **Figure 5 .** TEM micrographs of epoxy/DDS/MWNT nanocomposites
 253 (0.7 wt%) after a 5h dispersion with Rayneri (left) and after a dispersion with the 3 roll-mill calander (right)

254

255 Dense CNT agglomerates can be seen in **Figure** -left corresponding to the morphology of
 256 nanocomposite with the poorest dispersion state whereas individually dispersed nanotubes got with
 257 the 3 roll-mill calander are observed in **Figure** -right corresponding to the morphology of
 258 nanocomposite with the best dispersion state. As those observations allow only a qualitative
 259 evaluation of the dispersion, quantitative analyses were performed to assess what it means the terms
 260 “poorly dispersed” and “well dispersed” CNT-based nanocomposites. An image analysis was
 performed in order to compute a dispersion degree DD (defined between 0 and 100; 100 meaning a

261 dispersion only based on individually dispersed CNT) as well as a micron size agglomerate
 262 percentage $\mu_{\text{aggl}\%}$.

$$263 \quad DD = 100 \cdot P_{\text{tot}} / (P_{\text{CNT}} \cdot N_{\text{CNT}}) \quad (1)$$

264

265 With : P_{tot} : Sum of the projected perimeters of the whole particles seen on the micrograph

266 P_{CNT} : Mean projected perimeter of a CNT (504 nm)

267 N_{CNT} : Theoretical number of CNTs on the micrographs from the particles projected area

268 ($N_{\text{CNT}} = A_{\text{tot}} / A_{\text{CNT}}$)

269 A_{tot} : Sum of the projected areas of the whole particles seen on the micrograph

270 A_{CNT} : Mean projected area of a CNT (2880 nm²)

271 and

$$272 \quad \mu_{\text{aggl}\%} = A_{\text{micronic}} / A_{\text{theoretical}} \quad (2)$$

273 With : A_{micronic} : Sum of the projected areas of the micronic agglomerates seen on the micrograph

274 $A_{\text{theoretical}}$: The theoretical area of the CNT on the micrograph from the volumic filling rate
 275 in the nanocomposite

276

277 These discriminating parameters determined for different dispersion conditions are gathered in
 278 Table 1. No pre-dispersion means have been used to break the agglomerates before adding the amino
 279 hardener.

280

281 **Table 1.** Dispersion degree (DD) and micron size agglomerates percentage ($\mu_{\text{aggl}\%}$) for the different
 282 DGEBA/DDS/MWNT nanocomposites (0.7 wt%) processed in different conditions
 283 (standard deviation in brackets)

	No pre-dispersion	5 h Rayneri	20 h Rayneri	160 h Rayneri	240 h Rayneri	3 roll-mill
DD	4.9 (1.4)	10.6 (3)	28 (10.3)	42 (18.7)	44.9 (13.1)	74.5 (15.8)
$\mu_{\text{aggl}\%}$	73.3 (32.3)	36.9 (20.8)	16.1 (11.5)	14 (16.9)	13.4 (2.3)	2.2 (3.6)

284

285 These discriminating parameters which are relevant to quantify the dispersion states highlight that
 286 the Rayneri mixer is very relevant to improve the dispersion for short times (DD : +100 % and
 287 $\mu_{\text{aggl}\%}$: -50 % after 5 hours) but does not enhance drastically the dispersion state for very longer
 288 times of mixing. Residual micron-size agglomerates are very difficult to break and only the use of 3
 289 roll-mill calander allows to decrease $\mu_{\text{aggl}\%}$ significantly. By the combination of these analysis
 290 methods at different scales, extreme dispersion states have been generated and well characterized
 291 (with a DD from 5 to 75 and $\mu_{\text{aggl}\%}$ from 70 % to 2 %).

292

293 3.2-Impact of Carbon nanotubes dispersion state on the crosslinking kinetic

294

295 As montmorillonite [30, 31] or nanosilica [32], carbon nanotubes are well known to have a catalytic
 296 effect on the epoxy-amino condensation reactions by the presence of hydroxyl groups on external

297 walls [33-35]. As expected, this effect is more pronounced when the volume fraction of CNT increases
 298 or when this volume fraction is well dispersed. Let's consider the effects of CNT on the condensation
 299 kinetics performed on the reactive system based on DGEBA/DDS/MWNT with 0.7 % of MWNT by
 300 weight.

301

302 3.2.1.Epoxy conversion rate

303

304 Thanks to isothermal DSC measurements, the extent of reaction and the reaction rate were calculated
 305 (Figure 6) as proposed by Xie works [35].

306

$$\alpha = \frac{\Delta Ht}{\Delta Ht + \Delta Hr}$$

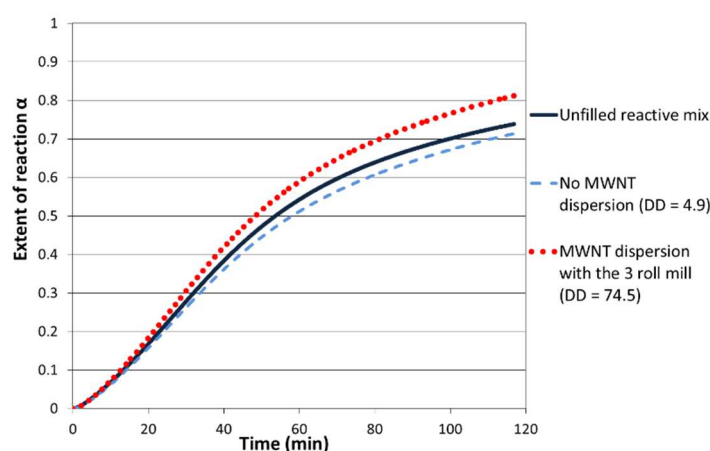
307 With : α is the advance of reaction (epoxy conversion)

308 ΔHt is the heat evolved up to a given time ($J.g^{-1}$)

309 $\Delta Ht + \Delta Hr$ is the total heat of reaction obtained from the isothermal and dynamic scan ($J.g^{-1}$)

310

311 After 2 hours at 150°C (first step of the curing cycle), the reaction kinetics for systems prepared with
 312 the 3 roll-mill calander pre-dispersion step is faster compared to the unfilled reactive one. On the
 313 other hand, the filled mixing without any dispersion step displays a reactivity quite similar to the
 314 neat epoxy one and even slightly lower. A clear difference in the cure kinetics is highlighted during
 315 the first step of the crosslinking reaction.



316

317 **Figure 6** . Extent of reaction (α) vs. time for a DGEBA DDS reactive system : without MWNT (continuous line)
 318 and filled with MWNT (0.7% in weight) with a different dispersion state (slashed line for the poor dispersion
 319 state and dotted line for the good dispersion state) at 150°C

320

321 The extent of reaction clearly depends of the MWNT dispersion state. After 2 hours at 150°C, α is
 322 higher than 80 % when the 3 roll-mill was used and is equal to 71 % in the case of a poor dispersion
 323 state. In this case α is even lower than the extent of reaction of the unfilled reactive system. An
 324 agglomerate-based morphology induces a downturn of the reaction kinetics whereas a good
 325 dispersion state has a catalytic effect on the crosslinking reaction.

326 It could be envisioned that some epoxy prepolymer remains confined in the MWNT agglomerates
 327 leading to a local modification of the epoxy/amine stoichiometric ratio, *i.e.* impacting reaction
 328 kinetics.

329

330 3.2.2. Activation energy of reaction in the presence of CNT

331

332 The Kissinger method [36] allows to determine the activation energy required for crosslinking
 333 reaction [37] from differential scanning calorimetry analyses (DSC) performed at different heating
 334 rates.

335
$$\frac{d(\ln(q/T_p^2))}{d(1/T_p)} = -\frac{E_a}{R} \quad (4)$$

336 With : q is the heating rate ($\text{K}\cdot\text{min}^{-1}$)

337 R is the constant of gases

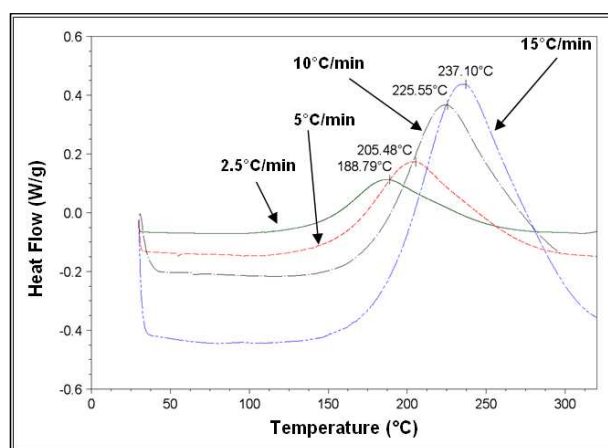
338 T_p is the temperature at the maximum of the exothermic peak (K)

339 E_a is the reaction activation energy ($\text{J}\cdot\text{mol}^{-1}$)

340

341 Figure 7 gives the DSC traces evidencing the exothermic peaks of the DGEBA/DDS systems for the
 342 different heating rates.

343



344

345 **Figure 7.** DSC analyses on reactive epoxy/amine (E/A) systems for different heating rates

346

347 The polymerization activation energies as a function of dispersion degrees of NTC within the
 348 epoxy/amine reactive system are reported in Table 2.

349

350

351

352

353

354 **Table 2** – Polymerization activation energies of the DGEBA/DDS reactive systems filled with MWNT (0.7 % by
355 weight) for different dispersion degrees (DD)

DD	Ea (kJ.mol ⁻¹)
Neat	71.9
4.9	71.1
10.3	70.7
28.35	69.4
47.6	69.4
74	65.9

356

357 The activation energy of the reactive system is lower in presence of MWNT whatever the dispersion
358 state compared with the neat epoxy-amine matrix. This decrease of the activation energy is enhanced
359 by a better quality of dispersion (up to 9% of difference between the dispersion obtained with the 3
360 roll-mill calander and the system without pre-dispersion).

361

362 3.2.2. Gelation time

363

364 Gelation time determination provides information about the catalytic effect of carbon nanoparticles
365 and their influence on the changes in physical behavior of the reactive system. The formation of a
366 chemical three-dimensional network leads to the appearance of an elastic response during
367 polymerization. The gelation time corresponds to the transition from a liquid state to a gel,
368 experimentally measured by chemio-rheological analyses from the crossover of the loss factor $\tan\delta$
369 vs. time during a multi frequency time sweep. Gel times are measured at 150°C on the reactive
370 systems based on DGEBA/DDS filled with 0.7 % of MWNT by weight tuned as a function of
371 dispersion state.

372 Figure 8 shows that the finest the dispersion, the shorter the gel time. On the opposite, an
373 agglomerated state leads to a longer gel time than one measured on the unfilled reactive system. This
374 observation can be explained once again by the confinement of a small quantity of prepolymer within
375 MWNT agglomerates that does not participate to the growing of the network, *i.e.* local changes of the
376 stoichiometric ratio are generated in and close to the CNT aggregates.

377

378

379

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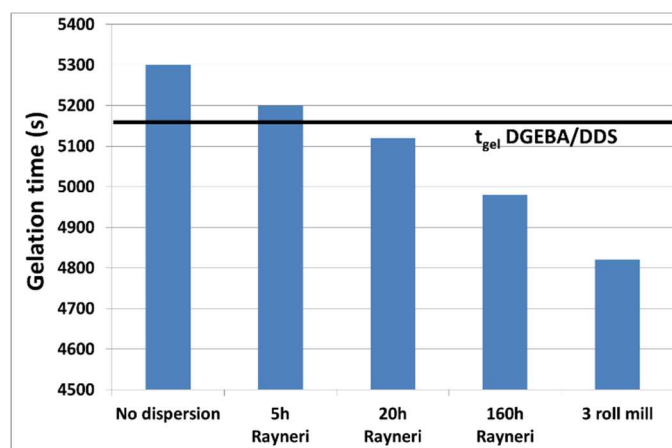


Figure 8. Gel time evolution as a function of the mixing conditions for the reactive system epoxy/amine/MWNT (0.7 wt%) at 150°C

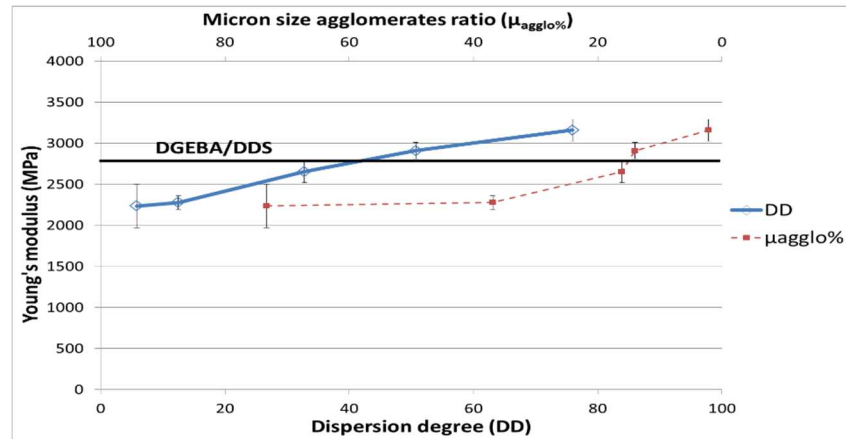
As a conclusion, it appears that the MWNT dispersion state has a pronounced influence on the epoxy-amine system polymerization. The catalytic effect of CNT is promoted by a good dispersion state whereas a poor dispersion induces a downturn of the crosslinking reaction.

3.3-Impact of CNT dispersion on the mechanical behavior of nanocomposites

The nanocomposites having a well-defined dispersion state were selected to study their mechanical behavior. Indirect and direct analyses were carried out in order to understand the stress transfer from matrix to CNT and between CNT in the aggregates or agglomerates.

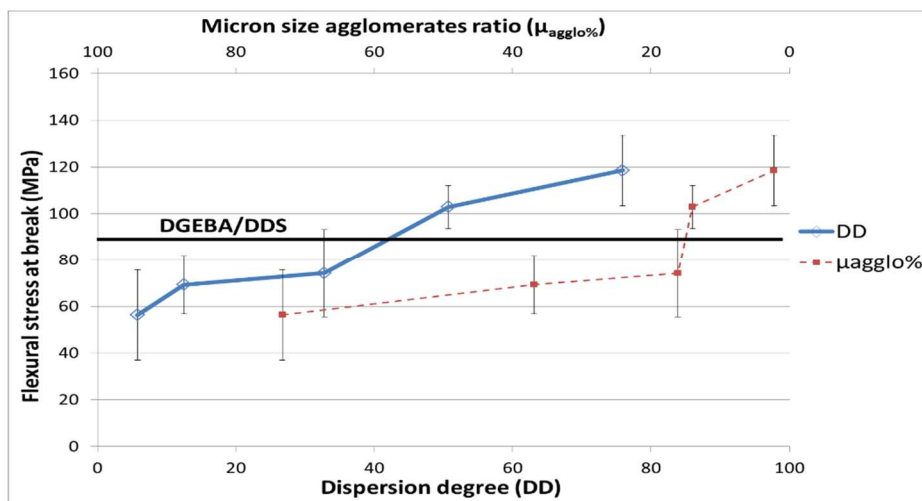
3.3.1 Macroscopic analyses

3 point bending tests carried out on nanocomposites are reported in Figure 9 and 10. As reported in the literature [12, 20, 22, 38], the mechanical properties are very sensitive to the dispersion state. Thus a poor CNT dispersion state ($DD = 4.9$) leads to a decrease of more than 20 % for the Young's modulus whereas the best dispersion state ($DD = 74.5$) leads to an increase of 10% compared to the neat epoxy network one. The stress at break is also very sensitive to the dispersion state since a decrease of 40 % with the poorest dispersion state and an increase of 35 % in the case of a good dispersion state are reported.



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Figure 9. Young's modulus as a function of MWNT dispersion degree in the DGEBA/DDS/MWNT nanocomposites (0.7 wt%)

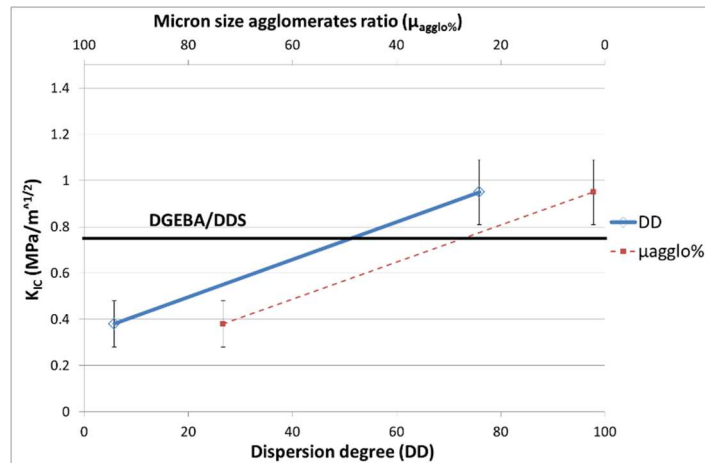


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Figure 10. Flexural stress at break as a function of MWNT dispersion degree in the DGEBA/DDS/MWNT nanocomposites (0.7 wt%)

414 The increase of the Young's modulus and of the flexural stress at break associated to a good
415 dispersion state of CNT can be explained by an efficient stress transfer at the CNT/polymer interface
416 as the CNT surfaces are fully in interaction with the epoxy network. On the other hand, the significant
417 decreases of these properties as the polymer matrix is filled with micronic MWNT agglomerates can
418 be explained by the poor cohesion of agglomerates that is only governed by the Van der Waals
419 interactions between MWNT. The fracture toughness of nanocomposites (
420 Figure 11) is also very sensitive to the dispersion state. K_{IC} decreases of 50 % with a poor dispersion
421 state and increases up to 22% for the best dispersion state (reached with 3 roll-mill) compared to the
422 neat epoxy network. A good dispersion state is required to take benefit from multiwall carbon
423 nanotubes on the mechanical properties of nanocomposites. Otherwise, an agglomerated
424 morphology can strongly reduce the mechanical properties of neat epoxy network. The decrease of
425 mechanical properties of nanocomposites compared to the neat network ones can be directly linked
426 to the non-polymerized DGEBA prepolymer confined in the CNT agglomerates and/or to non-
427 stoichiometric zones, as reported previously from reaction kinetics analyses.

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431 **Figure 11.** Fracture toughness (Critical stress intensity factor K_{1c}) as a function of the MWNT dispersion degree
 432 in the DGEBA/DDS/MWNT nanocomposites (0.7 wt%)

433

434 This reinforcing effect of CNT can be explained by the “crack-front pinning” process at the crack tip
 435 [38]. In such a process, the crack-front length increases as the crack meets rigid inclusions. As a
 436 consequence, this effect is magnified as the number of obstacles increases, *i.e.* in the case of a good
 437 dispersion state. If the MWNT are agglomerated, the number of objects decreases and their cohesion
 438 being weak (Van der Waals interactions), secondary cracks are generated.

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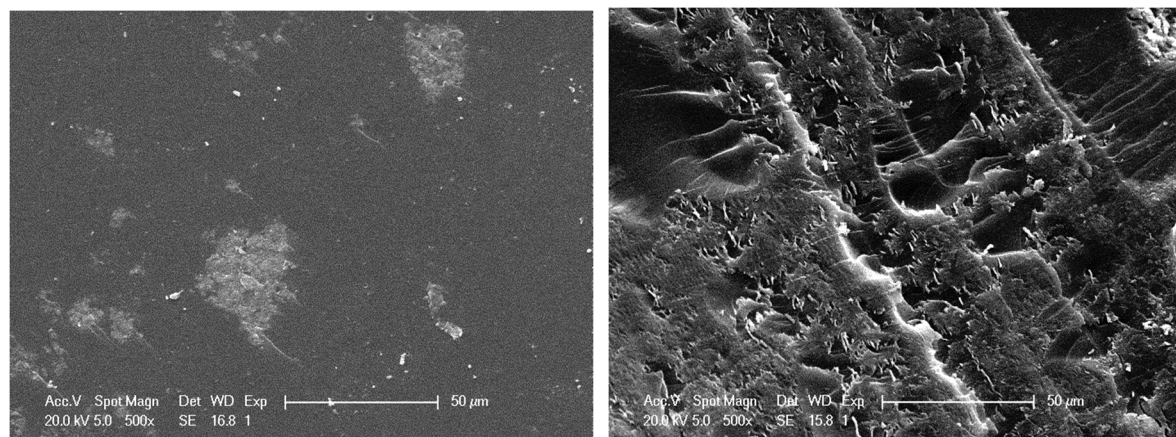
440 As a conclusion, it appears that as a small amount of MWNT is well dispersed in the matrix, the
 441 mechanical properties are significantly improved compared to the unfilled polymer but they can be
 442 seriously affected if the dispersion state is not good enough. In the first case, these are the
 443 CNT/polymer interactions which govern the behavior of well-dispersed CNT-based nanocomposites
 444 whereas in the second case, this is the level of interaction between CNT that governs the behavior of
 445 poorly dispersed CNT-based nanocomposites.

446

447 3.3.2. Analysis of interfacial interactions CNT/CNT vs CNT/matrix

448

449 Interfacial interactions with CNT can be also analyzed more locally from scanning electronic
 450 microscopy (SEM) and transmission electronic microscopy (TEM) on fracture surfaces.

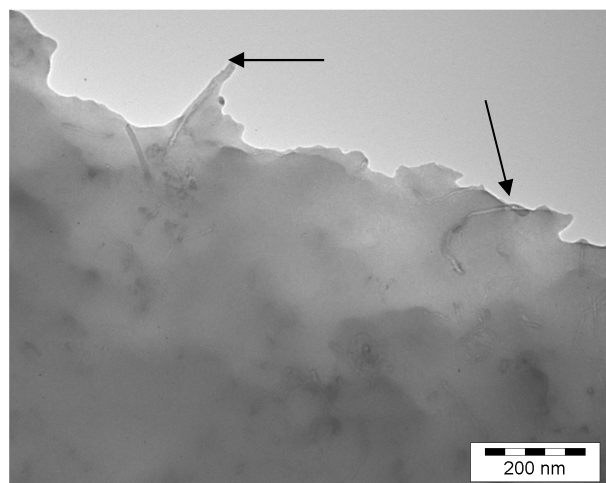


451
452 **Figure 12.** SEM Analysis on fractured surfaces of DGEBA/DDS/MWNT nanocomposites (0.7 wt%) with a poor
453 dispersion state, DD = 4.9 (left) and with a good dispersion state, DD = 74.5 (right)

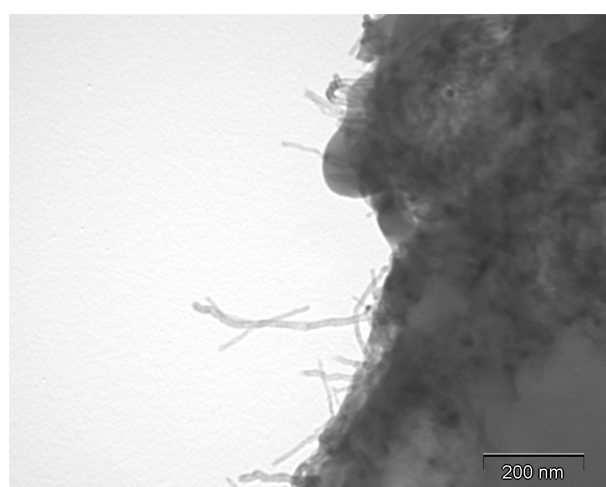
454
455 Epoxy networks typically exhibit a brittle fracture which can be characterized by a resulting mirror-
456 like fracture surface. The presence of MWNT aggregated under the form of agglomerates does not
457 modify so much the fracture surface of poorly dispersed CNT-based nanocomposites (Figure 12-left).
458 On the other hand, the toughening effect of well dispersed MWNT is clearly shown in SEM picture
459 (Figure 12-right). During failure, carbon nanotubes that are well wetted by the epoxy matrix induce
460 huge plastic deformation. As a consequence, the fracture toughness increases. The roughness of the
461 fracture surface and the presence of crack pinning are signatures of good interactions between
462 MWNT and epoxy matrix.

463
464 In order to go further into the investigations of fracture mechanisms, TEM micrographs were realized
465 on crack ends for the different materials (Figures 13).

466



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469

470 **Figure 13.** TEM micrographs on the fracture surfaces of DGEBA/DDS/MWNT nanocomposites (0.7 wt%).

471 above) after dispersion using a 3 roll-mill calander, below) without pre-dispersion

472

473 Individually dispersed CNT embedded in polymer matrix are clearly observed on fracture surfaces
474 of nanocomposite with a good dispersion state which is the signature of a good wetting (Figure 13-
475 above) and a strong interfacial adhesion. The rough fracture profile confirms the crack-front pinning
476 effect leading to the increase of the fracture toughness of the nanocomposite. On the other side, for
477 the poorly dispersed CNT-based nanocomposite (Figure 13 -below), MWNT are pull-out from the
478 polymer showing that they are not embedded by polymer matrix. The fracture surface is smooth and
479 regular even if the crack front meets a MWNT agglomerate. Its propagation front does not seem be
480 affected and stays straight (no toughening effect).

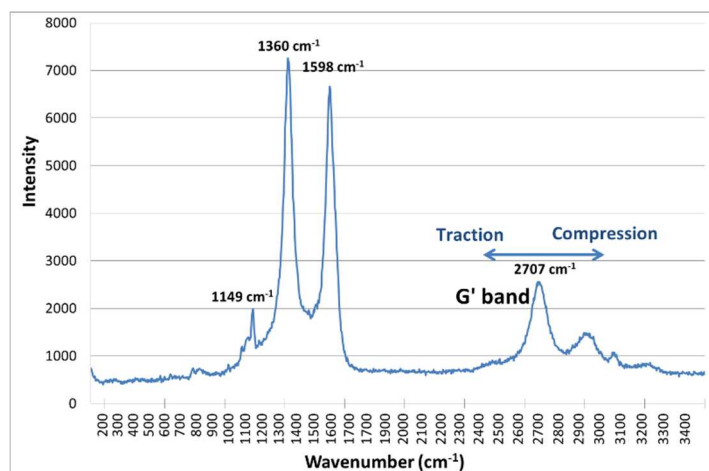
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482 From those electron microscopy observations, the interactions between CNT/CNT (in agglomerates)
483 and CNT/polymer appear clearly different, *i.e.* isolated CNT will require more energy to be extracted
484 from surrounding polymer than ones confined in an agglomerate.

485

486 Another experimental method to measure the level of the interaction between a CNT and the polymer
487 matrix is the micro-Raman spectroscopy. Previous works showed that the Raman spectra of carbon

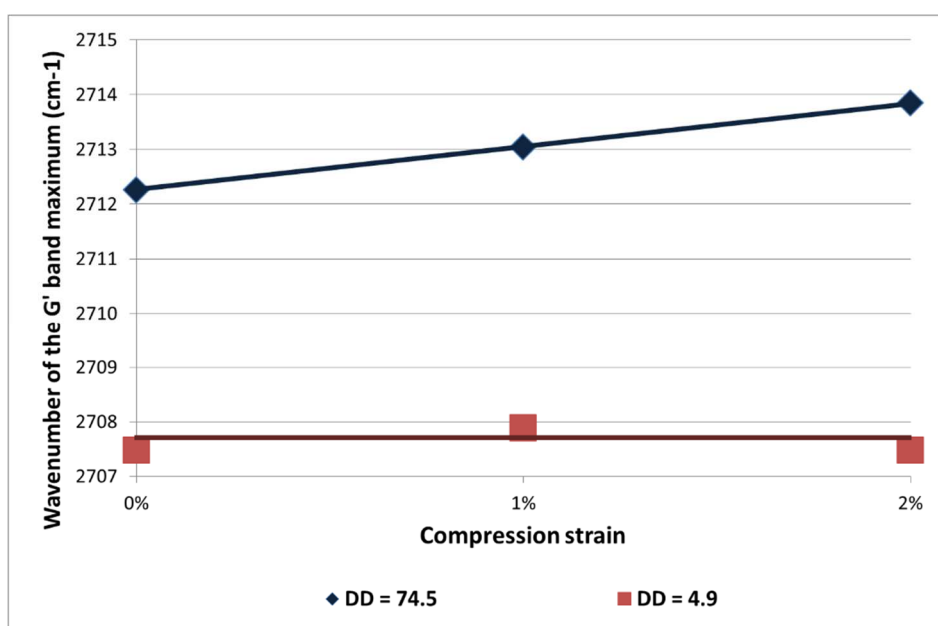
488 fibers were sensitive to the stresses induced in the fibers along their axis [39-40]. Thus the stress
 489 transfer between polymer matrix and CNT can be assessed by considering the shift of G' band ($2,700$
 490 cm^{-1}) in the nanocomposite submitted to a compression or traction load (
 491 Figure 14).
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495 **Figure 14.** Raman spectrum of a MWNT-based agglomerate in DGEBA/DDS/MWNT nanocomposite
 496 (0.7 wt%, DD = 4.9)

497
 498 Nanocomposites with very different dispersion states were placed under compression (1 % and 2 %
 499 of strain) and the G' band location was followed as a function of the MWNT dispersion state (as
 500 shown in Figure 15).
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504 **Figure 15.** G' band shift as a function of the compression strain of DGEBA/DDS/MWNT nanocomposite (0.7
 505 wt%) and of two different dispersion states (DD=4.9 and DD=74.5)

507 In case of well-dispersed CNT based nanocomposite under compression, a slight shift of the G' band
 508 is observed which means that MWNTs sustain compression thanks to a good stress transfer. In the
 509 case of nanocomposite with poorly dispersed CNT, no shift of the G' band is observed whatever the
 510 strain applied to the nanocomposite. MWNTs in agglomerates probably tend to be reorganized under
 511 the matrix deformation and only few CNTs sustain compression. Nevertheless, let's note that the G'
 512 band location in both extreme dispersions is very different even without applying compression. This
 513 can be explained by the polymer shrinking during the crosslinking applying an additional
 514 compression on individually dispersed MWNT.

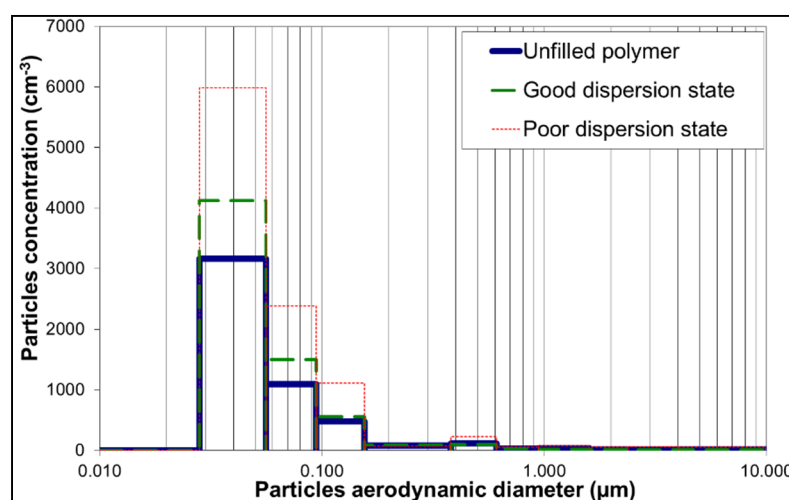
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516 3.4-Impact of CNT dispersion on the potential release ability

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518 Let's consider now the effect of the dispersion of fillers on the potential release ability during the
 519 nanocomposite life. The analysis of released particles investigated after simulating the wear
 520 undertaken by the material by using two tools either a brush or a rake is reported under form of size
 521 distribution in Figure 16 and 17. A releasing of ultrathin particles can be noted with a maximum
 522 diameter lower than 100 nm. The tool used has a non negligible influence on the releasing. The rake
 523 allows to release a higher concentration of nanoparticles (22600 cm^{-3}) with a much lower diameter (7-
 524 28 nm) in comparison with the brush (6000 cm^{-3}). This may be explained by the friction coefficient
 525 that is higher with the rake than with the brush applying an higher equivalent tensile stress from the
 526 Von Mises yield criterion. The hardness of material has also an influence on the stress applied by the
 527 tool on the sample and consequently on the releasing. The stiffness and the hardness of the glassy
 528 epoxy networks is prone to generate more particles with lower size (Wohlleben *et al* [41]).

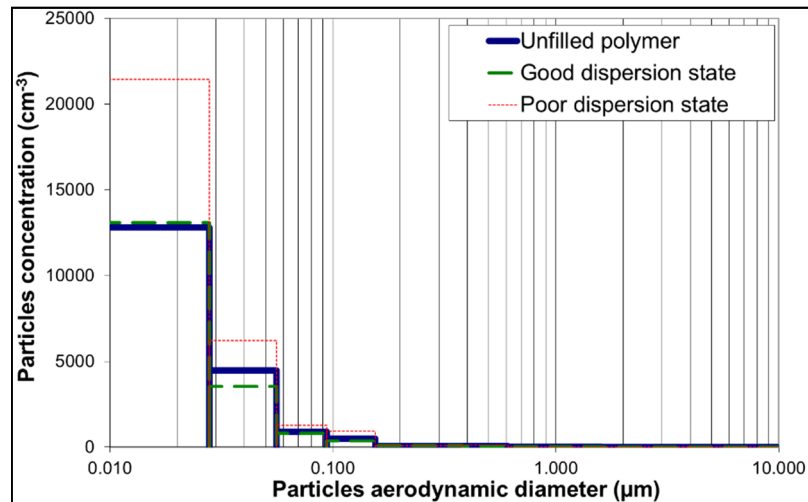
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531 **Figure 16.** Granulometric distribution of released particles during the use of the steel brush on DGEBA/DDS
 532 samples (ELPI data)

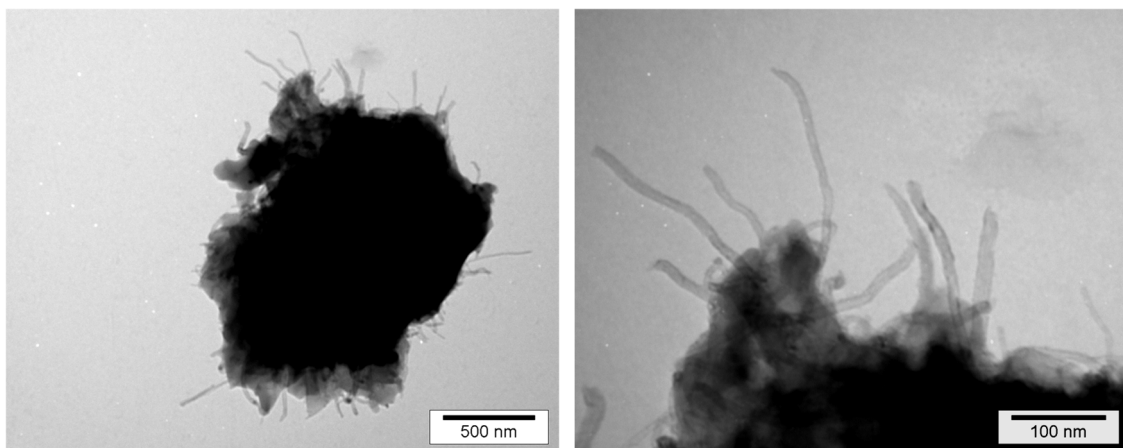
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Figure 17. Granulometric distribution of released particles during the use of the steel rake on DGEBA/DDS samples (ELPI data)

At the end, the dispersion state is a significant parameter on the granulometry of released particles. The nanocomposite with a bad dispersion releases much more nanofillers (between 50 and 70% fillers with the lowest diameters) than well dispersed or unfilled ones that display the same granulometric profile. The aggregates or agglomerates behave as defects favoring the crack propagation and initiation within the nanocomposite. Under the crack effect, the particles are released out of aggregates where the NTC are embedded into confined DGEBA prepolymer. Only aggregated particles with protruding fibers are observed in TEM picture reported in Figure 18 whereas free-standing CNTs were not observed.



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Figure 18. Released Particle after wear of DGEBA/DDS/MWNT (0.7 wt%) nanocomposite with a bad dispersion, DD = 4,9.

550 4-Conclusion

551 This paper aims at generating different dispersion states but in a controlled way of carbon nanotubes
552 into an epoxy-amine network. Two extreme morphologies are designed by varying the dispersion
553 tools, one with micron size agglomerates of aggregated carbon nanotubes characterized by a high
554 micron size agglomerates percentage and another one with individual carbon nanotubes embedded
555 into epoxy matrix, characterized by a high dispersion degree (DD). The dispersion state of carbon

556 nanotubes has an outstanding effect on the network build up : the gelation is catalyzed and the
557 conversion is enhanced when the carbon nanotubes are well dispersed. In the other case, epoxy
558 prepolymer can be confined into the carbon nanotubes aggregates locally modifying the epoxy –
559 amine stoichiometry preventing or delaying a total conversion. A well dispersed morphology is the
560 key architecture to reinforce the mechanical resistance of nanocomposite. Well embedded in the
561 surrounding polymer, the carbon nanotubes ensure a good load transfer towards the matrix. On the
562 contrary, a poor dispersion state with micron size CNT agglomerates has quite no influence on the
563 crack direction. If the crack front finds agglomerate on its path it just goes through considering the
564 weak agglomerate cohesion. There is no strong load transfer between CNT in agglomerate and the
565 mechanical properties of composites containing micronic agglomerates of MWNT can be much lower
566 than the initial properties of the unfilled polymer. After showing the huge influence of the NTC
567 dispersion on the polymerization mechanisms at macromolecular scale and on the macroscopic
568 behavior of nanocomposites, these works established a link between the nanocomposites
569 morphology and the potential release of carbon nanotubes during the nanocomposite life. We
570 checked experimentally that less energy is required to extract a CNT from an agglomerate than to
571 extract a CNT individually dispersed in the polymer matrix.

572

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