

1 **Electrorheological behaviour of suspensions in silicone oil of doped polyaniline**
2 **nanostructures containing carbon nanoparticles**

3 J. Santos^a, S. Goswami^b, N. Calero^a and M. T. Cidade^{b,*}

4 ^aUniversity of Sevilla, Chemical Engineering Department, C/ Profesor García
5 González,41012 , Sevilla, Spain

6 ^b Departamento de Ciência dos Materiais and CENIMAT/I3N, Faculdade de Ciências e
7 Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

8 *corresponding author. Email: mtc@fct.unl.pt

9
10 **Abstract**

11 Electrorheological (ER) fluids has been paying a lot of attention due to their potential use
12 in active control of various devices in mechanics, biomedicine or robotics. ER fluid
13 consisting of polarizable particles dispersed in a non-conducting liquid is considered to
14 be one of the most interesting and important smart fluids. This work presents the effect
15 of the dopant, camphorsulfonic acid (CSA) or citric acid (CA), on the eletrorheological
16 behaviour of suspensions of doped PANI nanostructures dispersed in silicone oil,
17 revealing its key role. The influence of carbon nanoparticles concentration has also been
18 studied for these dispersions. All the samples showed an ER effect, which increased with
19 electric field and nanostructures concentration and decreased with silicone oil viscosity.
20 However, the magnitude of this effect was strongly influenced not only by carbon
21 nanoparticles concentration but also by the dopant material. The ER effect was much
22 lower with a higher carbon nanoparticles concentration and doped with citric acid. The
23 latter is probably due to the different acidities of the dopants that leads to a different
24 conductivity of PANI nanostructures. Furthermore, the effect of the carbon nanoparticles
25 could be related to its charge trapping mechanism while the charge transfer through the

26 polymeric backbone occurs by hopping. PANI/CSA composite nanostructures dispersed
27 in silicone oil exhibited the highest ER activity, higher than 3 decades increase in apparent
28 viscosity for low shear rates and high electric fields, showing their potential application
29 as ER smart materials.

30 **Keywords:** Electrorheology, PANI nanostructures, ER smart materials, doped
31 polyaniline.

32

33 **1. Introduction**

34 Using external electric or magnetic fields to control the apparent viscosity of fluids has
35 been attracting much attention in scientific and technological fields because of the
36 potential use in active control of various devices in mechanics, biomedicine or robotics
37 (Han et al., 2007; Sims et al., 2000; Tsuchiya et al., 2004). This type of fluids can vary
38 their apparent viscosity reversibly responding to external electric or magnetic fields.
39 They are often referred as 'smart fluids' which include magnetorheological (MR) fluid,
40 electrorheological (ER) fluid, liquid crystal (as a case of ER fluids) and ferrofluids (as a
41 particular case of MR fluids). ER fluids consisting of polarizable particles dispersed in a
42 non-conducting liquid, are considered to be one of the most interesting and important
43 smart fluids (Wen et al., 2008). It can be transformed reversibly in just milliseconds from
44 a viscous state to an elastic state due to the disorder-order transition of particles under an
45 applied external electric field, showing tuneable changes in the rheological
46 characteristics. Under an applied electrical field, the polarizable particles orient along the
47 field direction and connect themselves in chains or in columnar structures that span the
48 space between the electrodes, which leads to tuneable changes in their rheological
49 characteristics (e.g., yield stress, shear apparent viscosity, shear modulus, etc.). Their
50 special rheological properties under the action of an external electric field makes ER fluid

51 possess potential uses to enhance the electric-mechanical conversion efficiency in
52 mechanical devices such as clutches, valves, damping devices, ink jet printer, human
53 muscle stimulator and mechanical sensor (Coulter et al., 1993; Hao, 2001).

54 For practical applications, a variety of polarizable particles, suspended in a non-
55 conducting medium, have been investigated as potential ER materials, the particles being
56 made of organic, inorganic, metallic, polymeric, and hybrid materials (Choi and Jhon,
57 2009; Dong et al., 2014; McIntyre et al., 2012; T Plachy et al., 2015a; Yin and Zhao,
58 2011). Due to its low density and its low abrasion to devices, organic ER systems have
59 been widely investigated in the past decades. Polyelectrolytes and semi-conducting
60 polymers are two kinds of important organic ER systems. The semi-conducting polymers
61 including polyaniline (PANI), have been frequently considered as ER active materials,
62 since the interfacial polarization, induced by the local drift of electrons or holes, provokes
63 their ER effect. PANI is considered a promising conducting polymer with a range of
64 advantages, such as outstanding electrical conductivity, well environmental stability,
65 relatively low cost, facile synthesis, and interesting electrical and optical properties
66 (Riede et al., 2000; Stěnička et al., 2011; Yun et al., 2011). Just one form of PANI possess
67 high conductivity: emeraldine (oxidised form). This is a p-type organic semiconductor
68 and its conductivity is favoured by dopant acid pHs. (Ghosh et al., 2003)

69 Some studies about ER effect of PANI hybridised with some inorganic materials, like
70 vanadium oxide (Goswami et al., 2014), clays (Yoshimoto, 2005), nanotubes (Choi et al.,
71 2005) and zeolites (Chattopadhyay et al., 2018) have been reported. For example, a recent
72 study about the influence of silicone oil viscosity on the ER effect of PANI hybridised
73 with graphene and tungsten nanoparticles has been published (Roman et al., 2018),
74 proving the importance of this parameter. Furthermore, there are some studies about ER
75 of PANI doped with HCl, which reveal the conducting properties of this polymer

76 hybridised with multiwalled carbon nanotubes or colloidal graphene oxide (Park et al.,
77 2005; Zhang et al., 2010). Nevertheless, the influence of different dopants or carbon
78 nanoparticles concentration on the ER effect of PANI nanostructures has not been
79 reported yet, which is the focus of this work and its novelty. There have been, however,
80 some papers dealing with this topic using various concentrations of dopants for other
81 conducting polymers or their oligomeric analogues (Stejskal et al., 2018). These works
82 report that the pyrrole/p-benzoquinone systems show ER effect if appropriate
83 concentrations of methanesulfonic acid are used. The same was also reported by Tomas
84 Plachy et al. for methanesulfonate salts of 2,5-(di-p-phenylenediamine)-1,4-
85 benzoquinone (T Plachy et al., 2015b).

86 The ER activity of the doped PANI including carbon nanoparticles-based systems has
87 been thoroughly studied in this work. The plausible explanations behind the ER properties
88 varying with different dopants, CSA and citric acid, and with the carbon particle
89 concentrations are presented in the current report. This system demonstrates its excellent
90 characteristics as a promising candidate in future ER fluid systems.

91 **2. Experimental section**

92 2.1. Synthesis of materials and preparation of the samples.

93 *Reagents and Materials*

94 Aniline monomer (Aldrich) was distilled under vacuum prior to use. Ammonium
95 persulfate (APS; 99.99%, Aldrich) and all other reagents like camphorsulfonic acid
96 (CSA; 98%, Sigma-Aldrich), citric acid (CA; $\geq 99.5\%$, Sigma-Aldrich), absolute ethanol
97 ($> 99.99\%$, Alfa Aesar) were used as received. Carbon nanoparticles collected from
98 candle shoot was used here.

99 *Synthesis of Materials*

100 The polymerization was done in 1:1 (v/v) ethanol-water media. Ethanol helped to disperse
101 the carbon nanoparticles within precursor during reaction and also slow down the
102 polymerization process to some extent. The synthesis was carried out following a typical
103 chemical oxidative polymerization of aniline at 0 °C (ice bath) in presence of APS as
104 oxidant and CSA or CA as dopant. Aniline was added to 20 mL of ethanol-water solution
105 and cooled at 0 °C . A pre-determined amount of carbon nanoparticles (1.1 and 2.2 mg
106 for 1 and 2 wt% sample preparations) was dispersed in 10 mL of ethanol-water mixture
107 by mechanical stirring and then APS (molar ratio, APS:Aniline 1:1) and CSA were added
108 to it. Dopant CSA or CA was used in 1 wt % of samples. After that, this mixture was kept
109 for cooling at 0 °C for few minutes and then was dropwise added to the precooled
110 monomer solution with 30 s shaking. The polymerization was allowed to continue for 1
111 h without any kind of disturbance to the system. The blackish green precipitate of carbon
112 nanoparticle incorporated doped polyaniline was collected after filtration and repeatedly
113 rinsed with DI water and methanol. The products were finally dried in a vacuum oven at
114 60 °C for 24 h to proceed on further investigations. The identification of the samples is
115 presented in table 1.

116 *Preparation of the samples*

117 All the samples were prepared by suspending the doped nanostructures in an insulating
118 silicone oil followed by ultrasonication. The kinematic viscosity of the silicone oils were
119 50 and 20 cSt. (Clearco Products Co. Inc., USA)

120 2.2. Characterization.

121 *Microscopy*

122 Morphological study of as synthesized nanostructures was carried out by field emission
123 scanning electron microscopy (FESEM-FIB, Carl Zeiss Auriga Crossbeam microscope).

124 The powder sample was casted on carbon tape to which a coating of 8 nm thin gold layer
125 was applied, so that no charge build-up can cause degradation of the image. Also the
126 operating voltage was kept low (5 kV) just to ensure the image quality.

127 *Rheological measurements*

128 Rheological experiments were conducted with a Bohlin Gemini HR^{nano} rotational
129 rheometer, coupled to a Bohlin ER cell using parallel plate (PP) geometry (isolated upper
130 plate, 40 mm diameter) and a high voltage generator (SPELLMANSL150). A gap of 250
131 μm was used during the oscillatory and steady state tests, with or without an applied
132 electric field, between the parallel plates.

133 Temperature equilibration time of 5 minutes was fixed for all experiments. Strain sweeps
134 at a frequency of 6.28 rad/s was performed for all systems studied to estimate the dynamic
135 linear viscoelastic range. Frequency sweep tests (from 0.5 to 20 rad/s) were performed
136 selecting a strain amplitude within the linear viscoelastic regime. Steady state
137 measurements were carried out from 0.01 s^{-1} to 1000 s^{-1} . After the temperature
138 equilibration but before starting the flow measurements, the samples were subjected to a
139 pre-shearing stage, with a pre-shear of 1 s^{-1} applied for 60 s, followed by an equilibration
140 time of 180 s. The influence of electric field applied on rheological properties was studied.
141 This electric field was applied in the direction perpendicular to the flow direction in the
142 range of $0\text{--}2\text{ kV mm}^{-1}$. This electric field was generated by applying a high voltage to
143 the gap between the plates with the DC power source while maintaining the voltage for 3
144 min for an equilibrium columnar structure prior to each ER measurement. All of the
145 aforementioned experiments were carried out at 25°C . To ensure the reproducibility of
146 the data, each of the measurements were conducted at least three times.

147 *Raman spectroscopy*

148 To study the chemical structures of the prepared products, Raman spectroscopy was
149 carried out with a Renishaw Qontor InVia Microscope with 532 nm excitation laser line
150 (using max 5 mW laser power and 1S exposure time for each 10 accumulations).

151 **3. Results and discussion**

152 Figure 1 represents the typical morphological features of the doped PANI sample
153 containing carbon nanoparticles. It shows that the nanostructures are formed with
154 particulate aggregates having rough surface.

155 [Insert figure 1]

156 The Raman spectra for PANICSA1-C1, PANICA1-C1 and carbon nanoparticles are
157 shown in Figure 2. The Raman of carbon nanoparticles shows two broad characteristic
158 bands at 1340 cm^{-1} (D-band) and 1571 cm^{-1} (G-band) which are corresponding to the
159 presence of amorphous disordered carbon structure of the nanoparticles. The Raman of
160 the carbon nanoparticle percolated PANICSA and PANICA systems present some typical
161 characteristic peaks of doped PANI with slightly shifted positions (Goswami et al., 2018;
162 Wu et al., 2015). The peaks at $1166\text{--}1171\text{ cm}^{-1}$ and $1589\text{--}1631\text{ cm}^{-1}$ can be attributed to
163 CH bending of the benzenoid ring and C=C stretching of the quinoid ring of PANI,
164 respectively. The band situated at 1245 cm^{-1} corresponds to CN stretching mode of the
165 single bonds, and the one at $1484\text{--}1497\text{ cm}^{-1}$ corresponds to CN stretching mode of the
166 quinoid units indicating the presence of doped PANI structure. The bands at $773\text{--}813$
167 cm^{-1} and $1404\text{--}1407\text{ cm}^{-1}$ are attributed to CH deformation and C=C stretching vibration
168 of the quinoid ring respectively. The peak at 1556 cm^{-1} is already depicting the shift of
169 the carbon particle related band within PANI matrix, showing the tight incorporation of
170 the carbon nanoparticles through $\pi\text{--}\pi$ synergy.

171 Figure 3A and 3B show the storage (G') and loss (G'') modulus in function of frequency
172 for A) PANICSA1-C1 and B) PANICA1-C1 dispersed in 20 cSt (19 mPa.s) silicone oil.
173 These viscoelastic functions represent the elastic and viscous components of a
174 viscoelastic material, respectively. G' and G'' are markedly dependent of frequency
175 without any electric field applied and G'' is higher than G' in all frequency range studied
176 for PANICA1-C1 suspension. Hence, its behaviour is liquid-like in absence of any field.
177 A similar nature is shown by PANICSA1-C1 suspension. G' and G'' increase with the
178 electric field applied and both nanostructures suspensions change to a solid-like character
179 upon application of the electric field. It is important to notice that for the same electric
180 field applied, G' and G'' for PANICSA1-C1 suspensions are much higher than for
181 PANICA1-C1 suspensions. This may be due to the different acidity constant of the acids
182 ($k_{CSA} = 10^{-1.2}$; $k_{CA} = 10^{-3.15}$) that provokes different conductivities and consequently,
183 polarization of the systems (Block et al., 1990). Since doped PANI is a p-type
184 semiconductor, its conductivity is due to the high mobility of the charge carriers (holes).
185 However, the only form of PANI that possesses high electrical conductivity is emeraldine
186 salt. This form is favoured by low pH. (Zuo et al., 1989), therefore, PANI doped with a
187 stronger acid will be more conductive and more polarizable than doped with a weaker
188 acid. CA is weaker than CSA meaning that there will be less PANI in emeraldine form.
189 The conductivities are 0.65 S/m and 0.28 S/m for PANICSA1-C1 and PANICSA1-C2,
190 respectively, while is 0.03 S/m for PANICA1-C1 system and 1.5×10^3 S/m for carbon
191 nanoparticles. In conclusion, even though the concentration of particles in the suspension
192 may be the same, the polarization is higher in PANICSA1-C1, which leads to a higher
193 ER effect in this case.

194 [Insert figure 3A and 3B]

195 Figure 4 shows apparent viscosity curves for A) PANICSA1-C1 and B) PANICA1-C1
196 dispersed in 20 cSt (19 mPa.s) silicone oil. All samples show a shear thinning behaviour
197 with a trend to reach a constant apparent viscosity value at high shear rates. An increase
198 of apparent viscosity with electric field applied is exhibited for PANICSA1-C1
199 suspension for all electric field strengths studied. However, the increase of apparent
200 viscosity for PANICA1-C1 suspension occurs only from 0.5 kV/mm on. Since the electric
201 field is perpendicular to the flow field, the particles reorient themselves in the direction
202 of the electric field forming chains or column structures if the flow field is not strong
203 enough to avoid it. This fact increases the apparent viscosity of the sample. At high flow
204 field strengths, which means high shear rates, the flow field became dominant over the
205 electric field leading to the destruction of the columns and to the corresponding apparent
206 viscosity decrease and all the curves tend to the curve without any electric field applied.
207 Furthermore, the shear rate for which a strong decrease in apparent viscosity is observed
208 depends on the electric field strength, meaning that at higher electric fields, higher shear
209 rates are necessary to overcome the effect of the electric field.

210 [Insert figure 4A and 4B]

211 To better analyse the different flow behaviours of the samples the apparent viscosity at
212 0.1 s^{-1} is presented in figure 5. There is a marked increase of the apparent viscosity with
213 electric field strength for 1wt% suspensions doped with CSA (PANICSA1-C1) in
214 comparison with those doped with CA (PANICA1-C1 and PANICA2-C1). The reason of
215 this difference is the aforementioned different acidity constant of the acids. Even when
216 doubling the carriers' concentration in case of PANICA suspension (PANICA2-C1), the
217 ER effect is still much higher for PANICSA1-C1 suspension, as seen in figure 5.

218 [Insert figure 5]

219 Figure 6A shows the flow behaviour of PANICSA samples as a function of carbon
220 nanoparticles concentration without electric field applied (PANICSA1-C0, PANICSA1-
221 C1 and PANICSA1-C2). The flow curves are quite similar; shear-thinning behaviour with
222 a trend to reach a Newtonian plateau for the highest shear rates. Hence, these samples
223 possess the same flow properties without electric field applied. However, the behaviour
224 is different when an electric field is applied (figure 6B and 6C). Figure 6B and 6C exhibit
225 the flow properties of the PANICSA samples as a function of carbon nanoparticles
226 concentration at 0.5 kV/mm and 1 kV/mm, respectively. Although the form of the flow
227 curves is the same, the values of apparent viscosity are really different at low and medium
228 values of shear rate. At higher shear rates, the samples exhibited the same apparent
229 viscosity. It is interesting to note that the addition of carbon nanoparticles provoked a
230 decrease of the ER effect. This decrease was more marked for higher carbon nanoparticles
231 concentrations. To better analyse the ER effect with carbon nanoparticles concentration,
232 figure 7 is presented. Figure 7A shows the apparent viscosity at 0.1 s^{-1} for PANICSA
233 nanostructures containing different concentrations of carbon nanoparticles (PANICSA1-
234 C0, PANICSA1-C1 and PANICSA1-C2).

235 [Insert figure 6A, 6B and 6C]

236 Figure 7A shows that there is a decrease in the ER effect with carbon nanoparticles
237 concentration. This could be explained by the fact that carbon nanoparticles act as charge
238 trapping centres within the conductive matrix of PANI. While travelling through the
239 polymeric backbone by hopping mechanism the charge carriers are momentarily trapped
240 within the carbon nanoparticles thus restricting their normal path for conduction. It means
241 that the polarizable nanoparticles are prevented from making stable columns, leading to
242 a reduction in apparent viscosity (Gurram, 2017).

243 It could be argued that the synthesis and doping process of the PANI is not complete due
244 to the presence of the carbon nanoparticles, however it is not so. Actually, the surface of
245 the carbon nanoparticles become passivated by the —NH_2 group rich aniline during in-
246 situ polymerization (Goswami et al., 2018) and the Carbon-PANI forms a synergetic
247 system through $\pi\text{—}\pi$ transitions. According to literature review, the conductivity of
248 conducting filler loaded polymer depends largely on the content of fillers. Carbon
249 particles exhibit percolation phenomenon. Though, there is a critical content depending
250 on which the final C-PANI system shows its electrically conductive behaviour. Below
251 this critical concentration, there is no continuous conductive network existing through the
252 matrix due to the large separations among the fillers (Zhang et al., 2007). Thus, at such
253 low carbon nanoparticles contents, the conductivity of the system depends mainly on the
254 conductivity of the polymer matrix, which in this case is doped PANI and therefore, the
255 conductivity depends on its doping level. The carbon nanoparticles behaving as islands
256 within the matrix act as charge trapping sites for the hopping charge carriers. Accordingly,
257 the polarizability of our composite ER suspension decreases in the presence of carbon
258 nanoparticles which justifies the continuous decrease of ER activity with the increase of
259 carbon nanoparticles concentration. This explanation is reinforced by the figure 7B.
260 Carbon nanoparticles show Higher ER effect which is consistent with the high
261 conductivity of pristine carbon. But, when they are incorporated in PANICSA system
262 (with a concentration below the critical one we mentioned before), the conductivity
263 follows the charge trapping mechanism and hence the ER activity decreases.

264 [Insert figure 7A and 7B]

265 The ER efficiency of PANICSA samples is shown as a function of the electric field in
266 figure 8, for different carbon nanoparticles concentration (PANICSA1-C0, PANICSA1-
267 C1 and PANICSA1-C2). The efficiency of each fluid has been determined from the value

268 of $(\tau - \tau_0) / \tau_0$, where τ and τ_0 are the shear stresses with and without the electric field at a
269 low shear rate (0.13 s^{-1}). The corresponding value of this parameter for each sample gives
270 the relative increase in its shear stress (hence, the apparent viscosity), with respect to the
271 applied electric field. The efficiency relates to the utility of the material in the practical
272 field. (Goswami et al., 2014) . There is an increase of efficiency with electric field
273 strength for all the systems, however, a marked decrease in efficiency with carbon
274 nanoparticles concentration is observed.

275 [Insert figure 8]

276 Figure 9 shows the influence of silicone oil viscosity and electric field on flow curves for
277 PANICSA suspensions containing 2 wt% of carbon nanoparticles (PANICSA1-C2).
278 Flow curve of 50 cSt system showed a higher limit Newtonian apparent viscosity than the
279 flow curve of its counterpart. This fact is due to the fact that the apparent viscosity of the
280 systems is related to the viscosity of the continuous phase at high shear rates. The same
281 fact is observed under the application of 2 kV/mm at high shear rates. By contrast, the
282 apparent viscosity for 50 cSt systems at low shear rates was slightly lower than the
283 apparent viscosity for 20 cSt system. To better distinguish the different trends, figure 10
284 shows the apparent viscosity at 0.1 s^{-1} for PANICSA1-C2 sample as a function of
285 continuous phase viscosity and electric field applied. The increase of the continuous phase
286 viscosity provoked a decrease in the ER effect. This fact is due to the increase of the
287 difficulty in the formation of columns or chains when the oil viscosity is higher.

288 [Insert figure 9 and 10]

289

290 **Conclusions**

291 Novel ER fluids with doped polyaniline nanostructures containing carbon nanoparticles,
292 dispersed in silicone oil have been characterized using steady state and low angle
293 oscillatory shear (SAOS) tests. The fluids showed an increase of viscoelastic properties
294 and apparent viscosity with the electric field applied, which are typical of ER fluids. The
295 dopant (CSA/CA) of the PANI nanostructures is a key factor. The higher the acidity, the
296 higher the ER effect. This is due to the concentration of emeraldine, the conductive form
297 of PANI. In order to control the conduction mechanism within PANI backbone carbon
298 nanoparticles were introduced as charge trapping centres. The addition of carbon
299 nanoparticles provoked a decrease in the ER effect. This can be attributed to the fact that
300 it is more difficult for this nanostructures to form columns in presence of carbon
301 nanoparticles because, acting as the charge trapping centres, basically they defer the
302 carrier conduction within PANI by hopping mechanism. Consequently, the ER efficiency
303 is higher for systems without carbon nanoparticles. Dynamic oscillatory tests in the linear
304 viscoelastic regime support the results obtained in the steady shear measurements. The
305 suspensions change their behaviour from fluid-like to solid-like, but in different degree.
306 The higher storage modulus value of the sample doped with CSA is due to the stiffer
307 columnar structures that are formed in samples with higher emeraldine concentration.
308 Finally, the influence of nanostructures concentration and oil viscosity on ER effect was
309 studied. The increase of nanostructures concentration provoked an increase of the number
310 of columns, leading to higher ER effect. By contrast, the increase of silicone oil viscosity
311 reduce the easiness of formation of columns provoking a reduction of ER effect.
312 Therefore, this work extend the knowledge about PANI based nanostructures and
313 demonstrate the important role of the dopant.

314

315 **Acknowledgements**

316 This work is funded by National Funds through FCT - Portuguese Foundation for Science
317 and Technology, Reference UID/CTM/50025/2013 and FEDER funds through the
318 COMPETE 2020 Programme under the project number POCI-01-0145-FEDER-007688.
319 J. Santos acknowledges the financial support received from V Plan Propio Universidad
320 de Sevilla. S.Goswami acknowledges funding from European Community H2020
321 program under grant agreement No. 685758 (Project 1D-Neon).

322

323 Authors declare that there are no conflicts of interest.

324

325 **References**

326 Block H, Kelly JP, Qin A, et al. (1990) Materials and mechanisms in electrorheology.
327 *Langmuir* 6(1). ACS Publications: 6–14.

328 Chattopadhyay A, Rani P, Srivastava R, et al. (2018) Electro-elastoviscous response of
329 polyaniline functionalized nano-porous zeolite based colloidal dispersions. *Journal*
330 *of Colloid and Interface Science* 519. Elsevier Inc.: 242–254. DOI:
331 10.1016/j.jcis.2018.02.066.

332 Choi HJ and Jhon MS (2009) Electrorheology of polymers and nanocomposites. *Soft*
333 *Matter* 5(8). Royal Society of Chemistry: 1562–1567.

334 Choi HJ, Park SJ, Kim ST, et al. (2005) Electrorheological application of
335 polyaniline/multi-walled carbon nanotube composites. *Diamond and related*
336 *materials* 14(3). Elsevier: 766–769.

337 Coulter JP, Weiss KD and Carlson JD (1993) Engineering applications of
338 electrorheological materials. *Journal of Intelligent Material Systems and Structures*
339 4(2). Sage Publications: 248–259.

340 Dong Y, Liu Y, Yin J, et al. (2014) Preparation and enhanced electro-responsive
341 characteristic of graphene/layered double-hydroxide composite dielectric
342 nanoplates. *Journal of Materials Chemistry C* 2(48). Royal Society of Chemistry:
343 10386–10394.

344 Ghosh P, Sarkar A, Ghosh M, et al. (2003) A Study on Hall Voltage and Electrical

345 Resistivity of Doped Conducting Polyaniline. *Czechoslovak Journal of Physics*
346 53(12): 1219–1227. DOI: 10.1023/B:CJOP.0000010586.93433.3a.

347 Goswami S, Brehm T, Filonovich S, et al. (2014) Electrorheological properties of
348 polyaniline-vanadium oxide nanostructures suspended in silicone oil. *Smart*
349 *Materials and Structures* 23(10). IOP Publishing: 105012.

350 Goswami S, Nandy S, Deuermeier J, et al. (2018) Green Nanotechnology from Waste
351 Carbon–Polyaniline Composite: Generation of Wavelength-Independent Multiband
352 Photoluminescence for Sensitive Ion Detection. *Advanced Sustainable Systems*
353 2(1). Wiley Online Library: 1700137.

354 Gurram SK (2017) Titanium doped Zinc. In: *Atomic Layer Deposition of Zinc Based*
355 *Transparent Conductive Oxides*. Stuttgart: BoD–Books on Demand, pp. 119–150.

356 Han Y-M, Kang P-S, Sung K-G, et al. (2007) Force feedback control of a medical
357 haptic master using an electrorheological fluid. *Journal of Intelligent Material*
358 *Systems and Structures* 18(12). Sage Publications: 1149–1154.

359 Hao T (2001) Electrorheological fluids. *Advanced Materials* 13(24). Wiley Online
360 Library: 1847–1857.

361 McIntyre EC, Yang H and Green PF (2012) Electrorheology of polystyrene
362 filler/polyhedral silsesquioxane suspensions. *ACS applied materials & interfaces*
363 4(4). ACS Publications: 2148–2153.

364 Park SJ, Park SY, Cho MS, et al. (2005) Synthesis and electrorheology of multi-walled
365 carbon nanotube/polyaniline nanoparticles. *Synthetic Metals* 152(1-3): 337–340.
366 DOI: 10.1016/j.synthmet.2005.07.261.

367 Plachy T, Mrlik M, Kozakova Z, et al. (2015a) The electrorheological behavior of
368 suspensions based on molten-salt synthesized lithium titanate nanoparticles and
369 their core–shell titanate/urea analogues. *ACS applied materials & interfaces* 7(6).
370 ACS Publications: 3725–3731.

371 Plachy T, Sedlacik M, Pavlinek V, et al. (2015b) The observation of a conductivity
372 threshold on the electrorheological effect of p-phenylenediamine oxidized with p-
373 benzoquinone. *Journal of Materials Chemistry C* 3(38). Royal Society of
374 Chemistry: 9973–9980. DOI: 10.1039/c5tc02119g.

375 Riede A, Helmstedt M, Riede V, et al. (2000) In situ polymerized polyaniline films. 2.
376 Dispersion polymerization of aniline in the presence of colloidal silica. *Langmuir*
377 16(15). ACS Publications: 6240–6244.

378 Roman C, García-Morales M, Goswami S, et al. (2018) The electrorheological
379 performance of polyaniline-based hybrid particles suspensions in silicone oil:
380 Influence of the dispersing medium viscosity. *Smart Materials and Structures*
381 27(7). IOP Publishing. DOI: 10.1088/1361-665X/aac245.

382 Sims ND, Stanway R, Johnson AR, et al. (2000) Smart fluid damping: shaping the
383 force/velocity response through feedback control. *Journal of intelligent material*
384 *systems and structures* 11(12). Sage Publications: 945–958.

385 Stejskal J, Bober P, Trchová M, et al. (2018) Oxidation of pyrrole with p-benzoquinone
386 to semiconducting products and their application in electrorheology. *New J. Chem*
387 42: 10167. DOI: 10.1039/c8nj01283k.

388 Stěnička M, Pavlínek V, Sába P, et al. (2011) Structure changes of electrorheological
389 fluids based on polyaniline particles with various hydrophilicities and time
390 dependence of shear stress and conductivity during flow. *Colloid and Polymer*
391 *Science* 289(4). Springer: 409–414.

392 Tsuchiya K, Orihara Y, Kondo Y, et al. (2004) Control of viscoelasticity using redox
393 reaction. *Journal of the American Chemical Society* 126(39). ACS Publications:
394 12282–12283.

395 Wen W, Huang X and Sheng P (2008) Electrorheological fluids: structures and
396 mechanisms. *Soft Matter* 4(2). Royal Society of Chemistry: 200–210.

397 Wu W, Pan D, Li Y, et al. (2015) Facile fabrication of polyaniline nanotubes using the
398 self-assembly behavior based on the hydrogen bonding: a mechanistic study and
399 application in high-performance electrochemical supercapacitor electrode.
400 *Electrochimica Acta* 152. Elsevier: 126–134.

401 Yin J and Zhao X (2011) Electrorheology of nanofiber suspensions. *Nanoscale research*
402 *letters* 6(1). Springer New York: 1.

403 Yoshimoto S (2005) A Commentary on ‘Synthesis and electrorheological properties of
404 polyaniline-Na⁺-montmorillonite suspensions’ by JW Kim, SG Kim, HJ Choi, MS

405 Jhon (Macromol. Rapid Commun. 1999, 20, 450–452). *Macromolecular Rapid*
406 *Communications* 26(11). Wiley Online Library: 857–861.

407 Yun J, Im JS, Kim H-I, et al. (2011) Effect of oxyfluorination on electromagnetic
408 interference shielding of polyaniline-coated multi-walled carbon nanotubes.
409 *Colloid and Polymer Science* 289(15-16). Springer: 1749–1755.

410 Zhang W, Dehghani-Sanij AA and Blackburn RS (2007) Carbon based conductive
411 polymer composites. *Journal of materials science* 42(10). Springer: 3408–3418.

412 Zhang WL, Park BJ and Choi HJ (2010) Colloidal graphene oxide/polyaniline
413 nanocomposite and its electrorheology. *Chemical Communications* 46(30): 5596–
414 5598. DOI: 10.1039/c0cc00557f.

415 Zuo F, Angelopoulos M, MacDiarmid AG, et al. (1989) AC conductivity of emeraldine
416 polymer. *Physical Review B* 39(6). APS: 3570.

417

418 **Figure Captions**

419

420 Figure 1. FESEM image of a typical doped PANI sample containing carbon nanoparticles.

421 Figure 2. Typical Raman spectra of carbon nanoparticles and as synthesized doped PANI
422 with Carbon particles inside.

423 Figure 3. Storage modulus (G' , solid points) and loss modulus (G'' , open symbols) as a
424 function of the frequency under different electric fields applied, for suspensions of
425 PANICSA1-C1 (A) and PANICA1-C1 (B).

426 Figure 4. Flow curves under different electric fields applied, for suspensions of
427 PANICSA1-C1 (A) and PANICA1-C1 (B).

428 Figure 5. Influence of the dopant, particles concentration of PANICA suspensions and
429 electric field strength on apparent viscosity at 0.1 s^{-1} for suspensions of PANI
430 nanostructures containing 1 wt% of carbon nanoparticles: PANICSA1-C1, PANICA1-C1
431 and PANICA2-C1.

432 Figure 6. Flow curves for PANICSA1-C0, PANICSA1-C1 and PANICSA1-C2
433 suspensions A) without electric field B) at 0.5 kV/mm C) at 1 kV/mm.

434 Figure 7. (A) Apparent viscosity at 0.1 s^{-1} for suspensions of 1 wt% PANICSA
435 nanostructures containing different concentration of carbon nanoparticles (PANICSA1-
436 C0, PANICSA1-C1 and PANICSA1-C2 suspensions) (B) Flow curves for 0.45 wt%
437 carbon nanoparticles suspension as a function of electric field.

438 Figure 8. Efficiency as a function of electric field for PANICSA1 samples containing 0,
439 1 or 2 wt% carbon nanoparticles.

440 Figure 9. Influence of silicone oil viscosity and electric field on flow curves for
441 PANICSA1-C2 suspension.

442 Figure 10. Influence of silicone oil viscosity and electric field on apparent viscosity at 0.1
443 s^{-1} for PANICSA1-C2 suspension.

444

445 Table 1. Nomenclature used for different samples as a function of PANI nanostructures
446 concentration, carbon nanoparticles and the dopant.

447

Samples	% PANI nanosctuctures	% Carbon nanoparticles	CSA	CA
PANICA1-C1	1	1	no	yes
PANICA2-C1	2	1	no	yes
PANICSA1-C0	1	0	yes	no
PANICSA1-C1	1	1	yes	no
PANICSA1-C2	1	2	yes	no

448

449