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In Situ Interfacial Polymerization: A Technique for Rapid Formation of Highly Loaded Carbon Nanotube#Polymer Composites

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1 **In-Situ Interfacial Polymerization: A Technique for Rapid Formation of Highly Loaded**
2 **Carbon Nanotube-Polymer Composites.**

3
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19

20 **Abstract**

21 Composites of polymers and organized carbon nanotube (CNT) networks have been proposed as next-
22 generation lightweight structural materials, yet polymer infiltration of CNT networks often results in
23 stress-concentrating heterogeneities, due to local CNT aggregation or incomplete infiltration. Herein, it
24 is demonstrated that dense CNT-polymer composites with tailored polymer distribution can be
25 obtained by interfacial polymerization (IP), performed *in-situ* within CNT networks. Three regimes of

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26 the *in-situ* interfacial polymerization (ISIP) process are identified: a reaction-limited regime where the
27 polymer forms beads on the CNTs; a uniformly-filled regime with polymer throughout the CNT
28 network; and a transport-limited regime where polymer only forms near the outer surfaces. Uniform
29 polyamide-CNT composite sheets obtained by this method have a Young's modulus of 31 GPa and a
30 tensile strength of 776 MPa, which is a two-fold increase compared to the pristine CNT sheets. Overall,
31 premature failure of the composites is attributed to large voids in the pristine CNT sheets, suggesting
32 that further improved mechanical properties can be achieved with a more homogeneous CNT network.
33 Nevertheless, the rapid rate and overall controllability of ISIP suggest its viability for formation of
34 polymers within CNT networks via roll-to-roll methods.

36 1. Introduction

37 CNT-polymer composites are promising materials for high-performance structural
38 applications, as they combine the high strength and low density of CNTs with the ductility and
39 versatility of polymers. Early research on CNT-polymer composites focused primarily on bulk
40 dispersion methods of CNTs in a polymer matrix, which only allows for the addition of low CNT
41 contents (on the order of a few wt.%), and therefore only gives slight enhancements in mechanical
42 properties relative to the polymer.^[1] Yet, advances in floating catalyst based chemical vapor
43 deposition (FC-CVD) of CNTs,^[2] have enabled the formation of CNT assemblies such as sheets^[3] or
44 fibers^[4] in a continuous fashion. As a result, there has been a strong interest in creating highly
45 loaded CNT-polymer composites using CNT yarns or sheets, particularly using manufacturing
46 techniques well-known in the fiber composites industry such as resin impregnation and curing.

47 High CNT content composites are most often obtained by infiltration of CNT networks with a
48 polymer solution or a polymer melt.^[5] However, direct polymer infiltration of CNT networks results
49 in composites with heterogeneous morphologies and poor mechanical properties, due to stress
50 concentrations at voids within the composite. These voids generally arise from CNT aggregation,
51 resulting polymer-rich regions, as well as from the differential mobility of polymer chains with

52 different lengths.^[5] Additionally, many polymers used for structural and aerospace applications, such
53 as aramids, feature low solubility in most common solvents and have high melting points, making
54 them incompatible with direct infiltration techniques. Other methods, in which solutions of
55 nanofibers such as aramids combined with CNTs, are cast to form a composite film, have been
56 explored.^[6] However, the composites obtained by this technique feature low CNT content (1.5-7.5
57 wt.%), due to the limited ability to disperse the CNTs and nanofibers in solution.

58 One approach to overcome infiltration limits of polymers in dense CNT networks is to first
59 infiltrate a monomer, and then polymerize the monomer *in-situ* by free-radical bulk
60 polymerization^[7-9] or electropolymerization.^[10-12] While the morphology of composites obtained
61 using this method is more uniform than in the case of polymer infiltration, the mechanical properties
62 of the final composites are usually inferior due to use of polymers with mechanical properties
63 unsuitable for high modulus and high strength applications, such as polystyrene, poly(methyl
64 methacrylate) or polyaniline.^[9,13] Moreover, chain-growth reactions, particularly bulk polymerization,
65 are usually slow with reaction rates on the order of $10^{-5} \text{ mol L}^{-1} \cdot \text{s}^{-1}$ and reaction times on the order of
66 hours or days.^[14] Therefore, toward manufacturing of structural CNT-polymer composites, it is highly
67 desirable to have a means of forming high-performance polymers rapidly within CNT networks.

68 Interfacial polymerization (IP) is a type of polycondensation reaction where a polymer is
69 formed at the interface between two liquids, each containing one or more reactive monomers.^[15]
70 The most common embodiment of IP consists of the formation of polyamides at the interface
71 between an aqueous solution containing a diamine monomer, and a water-immiscible organic
72 solvent containing an acid chloride (or acyl chloride) monomer. IP typically uses highly reactive
73 monomers; the reaction rate is $\sim 10^4\text{-}10^5 \text{ mol L}^{-1} \text{ s}^{-1}$, and films form in seconds.^[15] IP is used in fiber

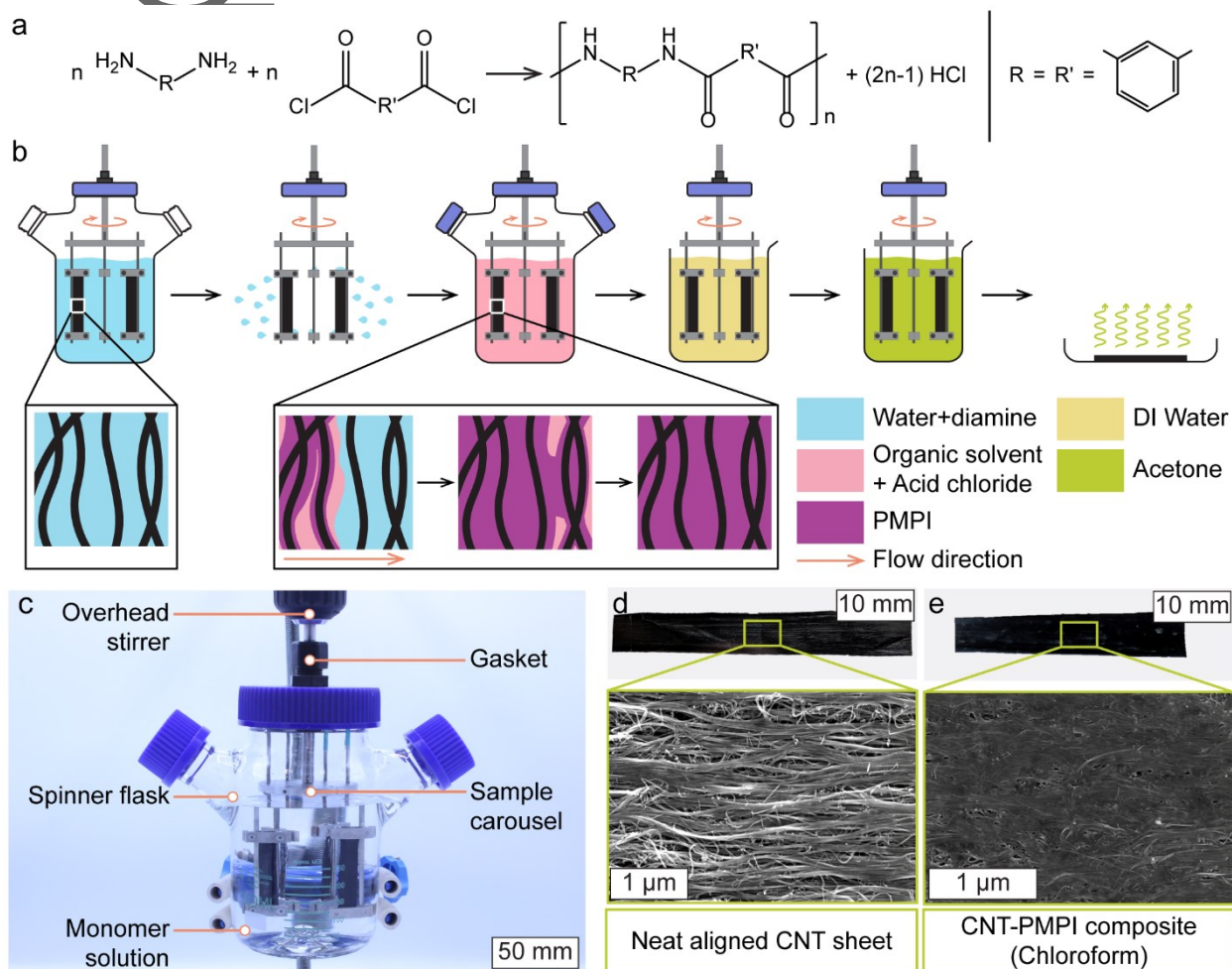
74 spinning,^[16] coating of fabrics in the textile industry,^[17] and the preparation of thin film composite
75 membranes for water desalination.^[18] By choice of the monomers and their functionality, IP can
76 result in a broad range of polymer types (e.g. polyamides, polyimides, polyureas) and morphology
77 (e.g. linear chains or crosslinked network). IP has also been used to form composites of CNTs with
78 aliphatic polymers, but this was done by dispersing CNTs in the organic solvent which limited the
79 CNT content of the final composite to ~1 wt%.^[19–21]

80 Herein, we present a versatile and scalable approach to manufacture dense CNT-polyamide
81 composites, via interfacial polymerization within CNT sheets. The choice of the organic solvent, and
82 the monomer concentrations, enable control of the polymer loading and distribution in the CNT
83 sheet. Using IP of poly(m-phenylene isophthalamide) (PMPI) as a model system, we combined
84 elemental analysis, electron microscopy, thermal analysis, uniaxial tensile testing and fractography
85 to identify the influence of monomer concentration and solvent type on the PMPI properties and its
86 spatial distribution within the CNT network. Building on these observations and the kinetics theory
87 of interfacial polycondensation, we provide insight on the design of the IP process in order to obtain
88 tunable morphologies, ranging from discontinuous polymer-coated CNTs to monolithic dense CNT-
89 polymer composites.

90 **2. Results**

91 To explore the use of ISIP for the formation of dense CNT-polymer composites, we used the
92 polycondensation reaction (Figure 1a) of a diamine monomer (dissolved in water) with an acid
93 chloride monomer (dissolved in a water-immiscible organic solvent). We chose R and R' to be meta-
94 phenyl groups because these groups are known to form π - π interactions with CNTs, which are
95 stronger than Van der Waals forces.^[5] The process is performed as follows (Figure 1b): a CNT sheet is
96 first immersed in an aqueous solution containing m-phenylene diamine. After a set time, the sheet is
97 removed from the solution, excess liquid is flung off, and then the sheet (still imbued with the
98 aqueous solution) is immersed in an organic solvent (chloroform or cyclohexanone) with dissolved
99 isophthaloyl chloride. The IP reaction occurs in the organic solvent at the liquid-liquid interface, and
100 polymer chains precipitate when reaching a critical length due to their low solubility in the organic
101 solvent. A custom-built reactor featuring a rotating carousel allowed the simultaneous immersion of
102 up to six CNT sheets in the reaction medium (Figure 1c). After removal, rinsing, and drying, PMPI is
103 found to be distributed in the CNT network (Figure 1d,e). The DC electrical conductivity of the CNT-
104 PMPI composites increases slightly compared to the neat CNT sheets (Figure S1a, b), indicating that
105 ISIP does not reduce the number of CNT-CNT contact points within the sheet, which would result in a
106 decrease of the conductivity. We attribute the increase in DC conductivity upon formation of PMPI
107 to the interplay of multiple factors. Polymer appears to precipitate preferentially around the contact
108 points between CNTs (Figure S1c), and we hypothesize that polymerization around CNTs at contact
109 points could result in a decrease in the contact resistance and therefore an increase in the overall
110 conductivity of the composite. Subsequently, with increasing monomer concentration, more PMPI is
111 produced at these locations and overall, resulting in a further conductivity increase of the

112 composite. Additionally, capillary forces could also cause slight densification of the CNT network
 113 upon infiltration of the solvent. However, further investigation is necessary to identify the exact
 114 influence of the identified phenomena on the electrical properties of the CNT-polymer composites.



115
 116 **Figure 1.** Polymer formation by interfacial polymerization in a CNT network. (a) Interfacial
 117 polycondensation reaction resulting in the formation of a polyamide. Herein, R and R' are both meta
 118 phenyl rings. (b) Schematic depicting the formation of a polyamide in a CNT network by interfacial
 119 polymerization. The nanoporous network is first immersed in an aqueous solution containing the
 120 diamine monomer. It is then transferred to an organic solvent containing the acid chloride
 121 monomer. The organic phase displaces the water phase and the acid chloride reacts immediately
 122 with the diamine, forming polyamide and a byproduct (hydrochloric acid). Rinsing steps remove
 123 impurities (unreacted monomer and byproduct) to result in a dense CNT-polymer composite. (c)

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124 Front-view of the ISIP reactor. (d,e) Optical and SEM images show the top view of CNT sheets (d)
125 before, and (e) after ISIP using chloroform as the organic solvent.

126

127 2.1. Key considerations for ISIP

128 To guide understanding of the relationship between synthesis conditions and final morphology, we
129 first present an interpretation of the mechanism of ISIP in CNT sheets. After the first immersion step,
130 the CNT network retains the aqueous solution of m-phenylene diamine within its porosity. Plunging
131 the water-saturated network in the organic phase results in interplay between the capillary-driven
132 flow through which the isophthaloyl chloride solution displaces the aqueous phase, and the polymer
133 formation and precipitation near the moving liquid-liquid interface (Figure 1b). Additionally, IP
134 occurs on the organic side of the interface; m-phenylene diamine molecules diffuse from the
135 aqueous phase into the organic solvent before reacting with the isophthaloyl chloride molecules. As
136 a result, the ISIP process involves two main governing rates (in $\text{mol L}^{-1} \text{s}^{-1}$):

137 ▪ $R_{trans} = R_{capi} + R_{diff}$ which encompasses the contribution of the capillary-driven
138 transport (R_{capi}) due to the motion of the liquid-liquid interface—influenced by relative
139 surface energies of the two liquids and the CNTs—and the diffusive term (R_{diff}) which
140 represents the diffusion of the diamine monomer through the liquid-liquid interface,
141 from the aqueous to the organic solution.

142 ▪ R_{rxn} which is the rate of the polycondensation reaction between m-phenylene diamine
143 and isophthaloyl chloride in the organic phase (Figure 1a).

144 The relative magnitudes of these two rates define the final morphology of the composite (Figure 2a).
145 On the one hand, to obtain uniform polymer loading, the rate of polymerization R_{rxn} must not be so
146 rapid such that the voids within the CNT network become obstructed with solid polymer before the
147 organic phase has fully imbibed the network. In the case where $R_{trans} < R_{rxn}$, we say the process
148 is “transport-limited”. On the other hand, if $R_{trans} > R_{rxn}$, the process is said to be “reaction-
149 limited” and the reaction may be so slow that polymer only partially fills the interior of the CNT
150 sheets after immersion times of ~minutes. In the case where the two rates are comparable
151 ($R_{trans} \sim R_{rxn}$), a uniform, dense composite can be obtained, with the polymer completely filling the
152 void space within the CNT network.

153 The imbibition kinetics through the network (captured by rate R_{capi}) depend on the characteristics
154 of the CNT network, including the CNT diameter distribution, packing density, and alignment. In this
155 study, we focused on aligned sheets of multi-walled CNTs (MWCNTs) obtained by a floating catalyst
156 CVD method^[22] (Figure 1c). The generally hydrophobic nature of MWCNTs^[23] and their resulting
157 stronger affinity with the organic solution than with the aqueous solution informed the sequential
158 order of the liquid phases in which the CNT sheets were immersed.

159 Additionally, R_{diff} depends on the miscibility of the organic solvent with water. A solvent featuring
160 higher water miscibility results in higher values of R_{diff} . From this perspective, to evaluate the
161 influence of the solvent water miscibility on the final composite morphology and properties,
162 composites made using chloroform (miscibility of 8.1g L⁻¹ in water at room temperature)^[24] and
163 cyclohexanone (miscibility of 87g L⁻¹ in water at room temperature)^[25] were compared.

164 For a given solvent, the rate-limiting step and therefore the final morphology can be adjusted by
 165 tuning the monomer concentration (Figure 2b).^[26] Assuming that the polymer precipitates
 166 immediately after the polymerization proceeds, we can consider that all the rates are equal to their
 167 initial value at $t=0$: $R_{trans}^o = R_{capi}^o + R_{diff}^o$ and R_{rxn}^o . We consider that both R_{diff}^o and R_{rxn}^o are
 168 dependent on the initial monomer concentrations of m-phenylene diamine $[NH_2]_o$ and isophthaloyl
 169 chloride $[COCl]_o$, while R_{capi}^o is a constant for a given solvent as it only depends on the surface
 170 energy of the organic phase. Additionally, we consider that both monomers are present in a 1:1
 171 molar ratio so that $[NH_2]_o = [COCl]_o = [M]_o$ as these conditions lead to the highest molecular
 172 weight polymer, according to reaction stoichiometry and experimental observations.^[15] From there,
 173 we can write the concentration dependence of the diffusivity rate as

$$R_{diff}^o = k_{diff} \frac{\Delta[M]_o}{d}$$

174 where k_{diff} is the rate constant characteristic of the diffusion of diamine from the aqueous solution
 175 to the organic solution, d is the diffusion distance at the liquid-liquid interface, and $\frac{\Delta[M]_o}{d}$ is the
 176 gradient of monomer concentration between the aqueous phase and the organic phase. Considering
 177 there is no diamine in the organic solution initially, and that d is a constant, we write:

$$R_{diff}^o = k_{diff} \frac{[M]_o}{d} = k_{diff,eff} [M]_o$$

178 In this case, $k_{diff,eff}$ is determined by the solvent type.

179 Next, the dependence of polymerization reaction rate on monomer concentration $[M]_o$ can be
 180 written according to the kinetics established for the polymerization reaction. We consider that




181 polymer forms through the self-catalyzed reaction mechanism^[26] of addition-elimination (Figure S2).
 182 First, a nucleophilic attack occurs on the positively-charged carbon atom in the acyl chloride
 183 functional group by the lone pair on the nitrogen atom in the amine functionality. Then, the carbon-
 184 oxygen double bond reforms and a chloride ion is pushed off and recombines with the hydrogen ion
 185 from the nitrogen to form HCl. From there, we can write:^[26]

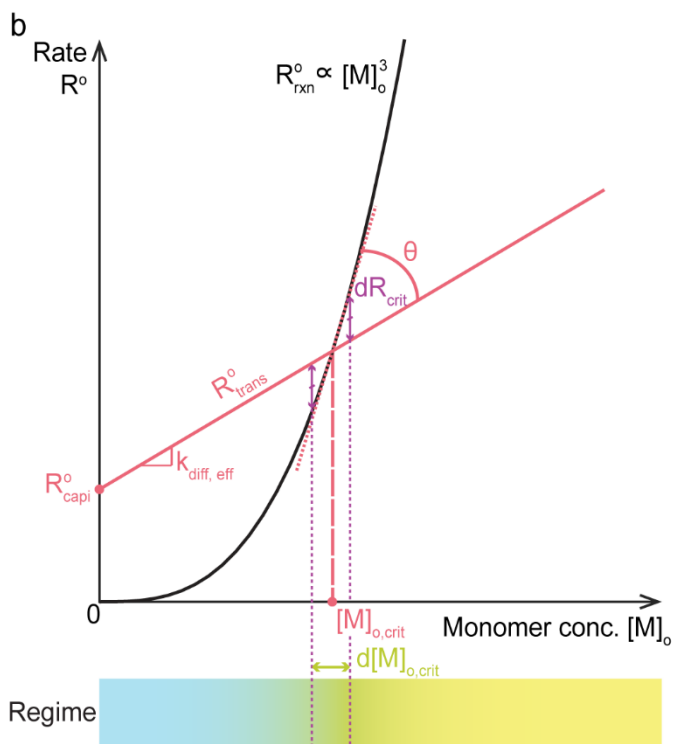
$$R_{rxn}^o = k_{rxn}[NH_2]_o[COCl]_o[COCl]_o = k_{rxn}[M]_o^3$$

186 Here, k_{rxn} is the rate constant of reaction and is assumed to be independent of solvent type.
 187 Qualitatively, in Figure 2b we show how R_{rxn}^o and R_{trans}^o depend on $[M]_o$. The concentration range
 188 $d[M]_o^{crit}$ near $[M]_o^{crit}$, within which both rates are comparable and uniform polymer composites can
 189 be obtained, depends on the angle θ between the curve R_{rxn}^o and the R_{trans}^o line at $[M]_o^{crit}$. For a
 190 uniform loading of polymer to be created, the difference between R_{rxn}^o and R_{trans}^o must be less
 191 than some finite value dR_{crit} . The range of concentrations amenable to this regime decreases as θ
 192 increases. Qualitatively, for large values of θ , the parameter range giving uniform polymer loading
 193 may be difficult to assess experimentally, as a small change in $[M]_o$ immediately results in a direct
 194 transition from the transport-limited regime to the reaction-limited regime. As θ is directly related
 195 to the slope and intercept of R_{trans}^o , it is determined by solvent type.

196 The present study focuses on varying monomer concentration to identify the different kinetic
 197 regimes for the two chosen organic solvents, specifically cyclohexanone and chloroform, and relates
 198 the rate-limiting step to the final morphology and mechanical properties of the obtained CNT-PMPI
 199 composites. In what follows, we first combine electron microscopy, elemental analysis and
 200 thermogravimetric analysis to identify the different kinetic regimes associated with the ISIP

201 conditions, as well as the nature of the polymer formed and the CNT-PMPI interaction. Second, we
 202 focus on assessing the multiscale morphology of the composites and its influence of the final
 203 mechanical properties of the CNT-PMPI composites obtained in the defined kinetics regimes.

a	Regime	Condition	Morphology
	Reaction-limited	$R_{trans}^o > R_{rxn}^o$	
	Uniformly-filled	$R_{trans}^o \sim R_{rxn}^o$	
	Transport-limited	$R_{trans}^o < R_{rxn}^o$	



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205 **Figure 2.** Relative rate dependence and resulting final composite morphology. (a) Definition of the
206 different kinetics regimes based on the relative magnitudes of the transport rate and the reaction
207 rate, as well as the expected resulting morphology. (b) Qualitative representation of the dependence
208 of the different rates involved in ISIP on monomer concentration.

209

210 **2.2. Assessment of polymer content variation and rate-limiting step**

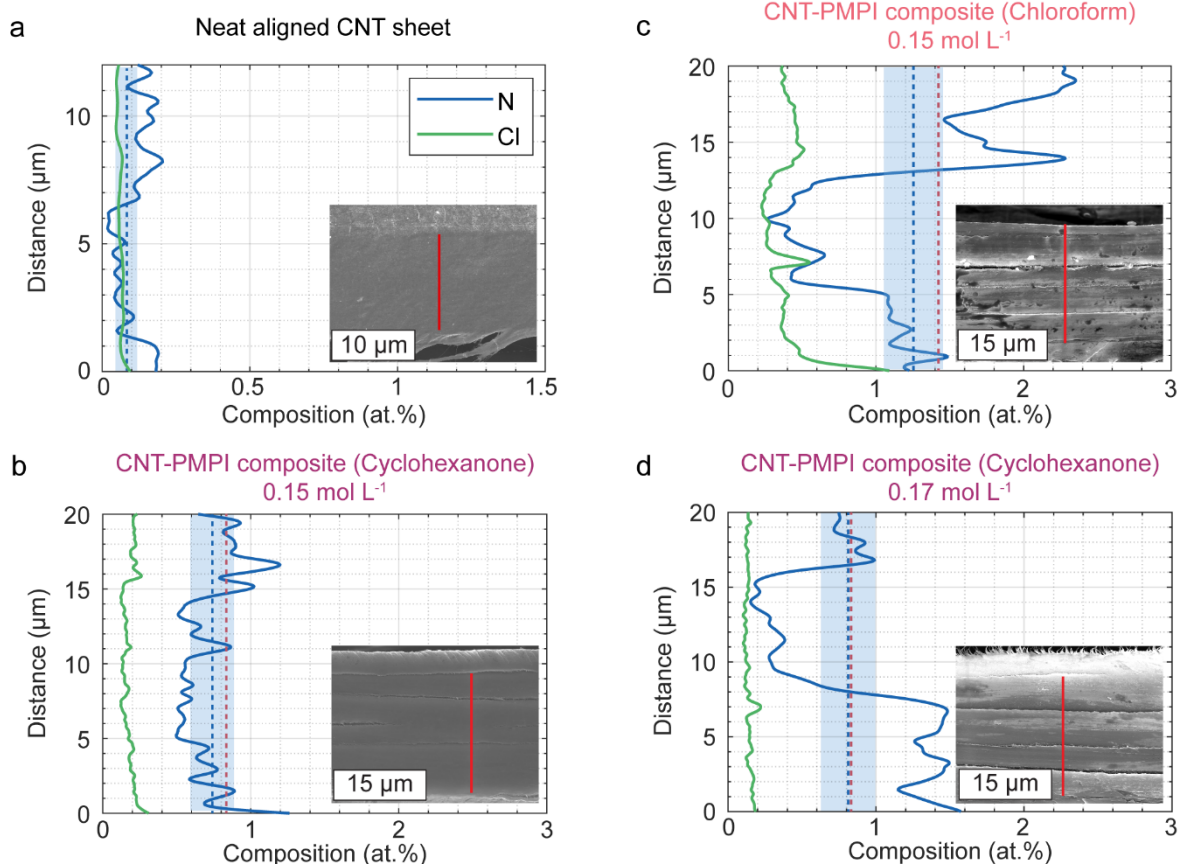
211 Guided by kinetics theory, we now show how to produce CNT-polymer composites with tailored
212 polymer morphology by ISIP. This is accomplished by adjusting the relative magnitudes of the
213 transport and reaction rates by varying the solvent type and $[M]_0$.

214 Energy Dispersive X-Ray Spectroscopy (EDS) was used to assess polymer content variation
215 throughout the thickness of the CNT composites (Figure 3), as well as the presence of potential
216 byproducts or residual solvent. Neat CNT sheets show nitrogen (N) and a chlorine (Cl) content on the
217 order of 0.1 ± 0.01 at.% (Figure 3a), allowing us to use the N signal as a measure of the polymer
218 content versus depth. Additionally, the Cl signal increases between the neat CNT sheets and the
219 CNT-PMPI composites (Figure 3b-d), particularly in the case where chloroform is used as the solvent.
220 This increase is attributed to the amount of residual by-product (HCl) and chloroform trapped in the
221 polymer, which could not be washed off nor evaporated due to the dense and tortuous CNT-PMPI
222 composite structure.

223 CNT-PMPI composites obtained with cyclohexanone and chloroform at equivalent monomer
224 concentration (0.15 mol L^{-1}) exhibit very different spatial distributions of the polymer content
225 throughout the thickness of the CNT sheet. The CNT-PMPI composite formed with cyclohexanone
226 shows a constant polymer loading throughout the thickness (Figure 3b), indicating that a $[M]_0$ of

227 0.15 mol L⁻¹ resulted in $R_{trans}^{cyclo} \geq R_{rxn}^{cyclo}$, i.e., the reaction-limited or uniformly-filled regime as
228 defined in Figure 2a. The uniformity of polymer distribution is further confirmed by 2D EDS mapping
229 (Figure S3 and Table S1). Conversely, IP using chloroform produces a gradient of polymer content,
230 decreasing toward the center of the CNT sheet. (Figure 3c). This suggests that the same $[M]_o$
231 resulted in $R_{trans}^{chloro} < R_{rxn}^{chloro}$ i.e., the transport-limited regime.

232 This observation is explained by the dependence of solvent transport rate on its miscibility with
233 water. Cyclohexanone features a water miscibility 20 times greater than chloroform, resulting in
234 faster diffusion of m-phenylene diamine through the interface. From this perspective, the slope of
235 R_{trans}^o with $[M]_o$ is greater in the case of cyclohexanone (Figure 2b) and the uniformly-filled regime
236 occurs at a higher $[M]_o^{crit}$. However, for $[M]_o=0.17$ mol L⁻¹ in cyclohexanone, non-uniform polymer
237 distribution is obtained (Figure 3d) indicating that the increase in monomer concentration results in
238 $R_{trans}^{cyclo} < R_{rxn}^{cyclo}$, i.e. the transport-limited regime is reached. Transmission Electron Microscopy
239 (TEM) images (Figure 4) of a thin (~60 nm) cross-section of a CNT-PMPI composite obtained in
240 cyclohexanone at $[M]_o=0.15$ mol L⁻¹, also suggest uniform polymer loading throughout the thickness
241 of the sheet with no apparent residual voids (Figure 4a). Nevertheless, the large amount of polymer
242 and the thickness of the cross-section in those conditions does not enable high-resolution imaging
243 and assessment of the crystallinity of the PMPI formed by ISIP. From this perspective, cryo-FIB was
244 performed to isolate lamellae from the core of CNT-PMPI composites obtained in the transport-
245 limited regime. Those lamellae exhibit lower polymer content and enable high-resolution TEM
246 images of isolated CNTs and PMPI (Figure 4b), showing that PMPI synthesized by ISIP forms an
247 amorphous solid coating on the CNTs, which prevents the observation of the crystalline planes of the
248 CNT walls by TEM (Figure 4c).



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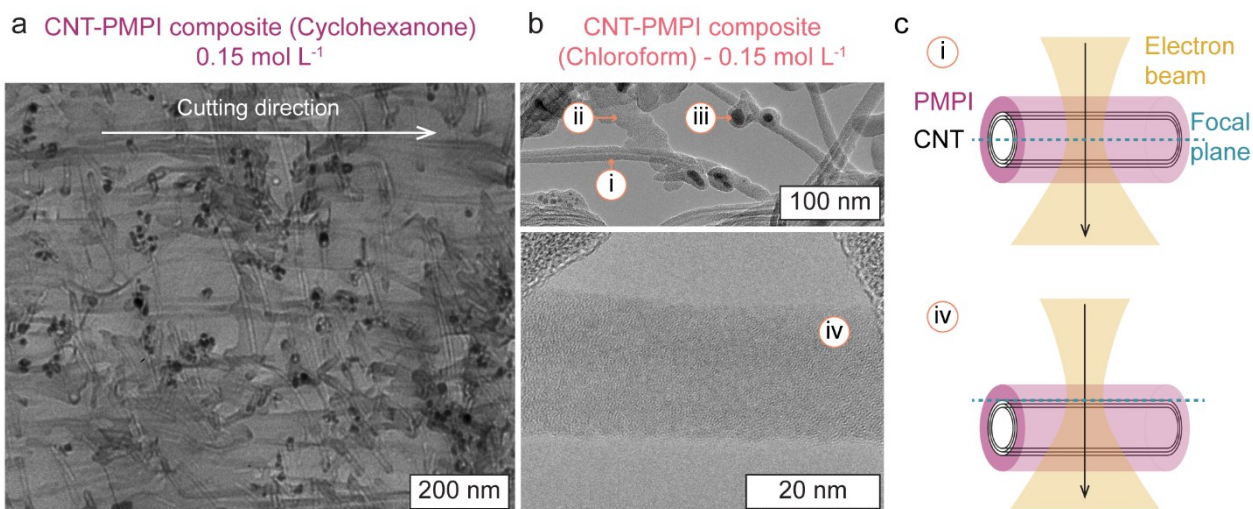
250 **Figure 3.** EDS line profile through the cross-section of (a) the bare CNT sheet, and (b-d) composite
 251 sheets obtained using $[M]_o = 0.15 \text{ mol L}^{-1}$ in (b) cyclohexanone and (c) chloroform as the organic
 252 phase, and (d) $[M]_o = 0.17 \text{ mol L}^{-1}$ in cyclohexanone. Nitrogen is one of the main elements that is
 253 present in the polymer chain, but not in the CNTs. Chlorine is the result of residual hydrochloric acid
 254 or chlorinated solvent in the system. The blue dashed line indicates the average at.% of nitrogen
 255 while the shaded area is the error of the EDS measurement. The red dashed line is the expected at.%
 256 N calculated from TGA measurements. Inset images show scanning electron micrographs of the
 257 cross-sections of the relevant samples and the red lines show where the EDS scans were performed.

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261 **Figure 4.** TEM images of CNT-PMPI composites. (a) Microtome section of a CNT-PMPI composite
 262 showing uniform PMPI loading. Compression and shear during the cutting process result in some
 263 CNTs aligning along the cutting direction. (b) TEM view of a CNT-PMPI lamella obtained by Cryo-
 264 Focused Ion Beam (FIB) from a composite sample formed in chloroform. (i) A sheath of PMPI formed
 265 around a single CNT, (ii) neat PMPI bridging between CNTs, and (iii) a residual iron catalyst particle
 266 embedded in PMPI. (iv) Higher magnification of the PMPI-wrapped CNT shows the pattern typical for
 267 amorphous material. (c) Schematics explaining the different appearance in TEM images of PMPI-
 268 wrapped CNTs, depending on the focus of the electron beam. Regardless of the beam focus location,
 269 the crystalline planes of the CNT walls cannot be resolved due to the amorphous nature of the PMPI
 270 coating. When the electron beam is focused on the center of the CNT, a higher brightness line can be
 271 seen as the hollow center of the CNT as seen in (i). When the electron beam is focused on the
 272 surface of the CNT, the amorphous texture of the polymer dominates, and the CNT wall crystalline
 273 planes cannot be resolved, as seen in (iv).

274

275 2.3. Thermal stability of *in-situ* polymerized polyamide and the effect of CNTs

276 Thermogravimetric analysis was used to assess the thermal stability of PMPI synthesized by ISIP, as
 277 well as the polymer content in the final CNT-PMPI composite (Figure 5). PMPI, as well as the CNT-
 278 PMPI composites, show a significant mass loss beginning at around 400°C, corresponding to the
 279 decomposition of PMPI (Figure 5a). Note that in its neat form, the decomposition profile of PMPI is
 280 independent of solvent type and monomer concentration used in the IP process.

281 The relationship between polymer content and $[M]_o$ is strongly influenced by the organic solvent
282 used for ISIP (Figure 5b). For cyclohexanone, the polymer content increases with $[M]_o < 0.15 \text{ mol}$
283 L^{-1} , then remains constant at higher concentrations. In the case of chloroform, the polymer content
284 increases monotonically with $[M]_o$ (from 0.075 to 0.28 mol L^{-1}). By EDS, we find that CNT-PMPI
285 composites obtained in chloroform solutions with $[M]_o \geq 0.1 \text{ mol L}^{-1}$ feature non-uniform polymer
286 loading, indicating the transport-limited regime at these concentrations. Similarly, we find that CNT-
287 PMPI composites obtained in cyclohexanone solution with $[M]_o \geq 0.17 \text{ mol L}^{-1}$ also fall within the
288 transport-limited regime of the ISIP process.

289 Compared to neat PMPI synthesized by IP in absence of CNTs, CNT-PMPI composites show a
290 dependence of the onset temperature of thermal degradation T_{onset} with monomer concentration
291 and solvent type (Figure 5c). In the reaction-limited regime (cyclohexanone with $[M]_o < 0.15 \text{ mol}$
292 L^{-1}), T_{onset} increases with $[M]_o$ and is greater than T_{onset} of neat PMPI. The increase in T_{onset} can be
293 influenced by both the polymer loading, as well as variations in polymer characteristics (density,
294 ordering) due to the presence of CNTs. First, in the reaction-limited regime, an increase of $[M]_o$
295 results in more PMPI being formed between the CNTs at otherwise identical IP conditions, i.e., a
296 higher polymer content overall. We hypothesize that the greater polymer content impedes diffusion
297 of decomposition by-products from the CNT sheet, imparting a higher measured onset temperature.
298 As such, CNT-PMPI composites showing uniform polymer loading (cyclohexanone and $[M]_o$ of 0.15
299 mol L^{-1}) exhibit the highest measured T_{onset} . Chloroform does not show a uniformly-filled regime in
300 the range of concentrations tested. Second, in the transport-limited regime, T_{onset} decreases
301 linearly with $[M]_o$, reaching values lower than that of neat PMPI, suggesting that CNT-PMPI
302 interaction also influences T_{onset} . In addition, the slope of the decay is independent of the solvent

303 used for ISIP, suggesting that the CNT-PMPI interaction is governed by the chemical structure of the
304 polymer, regardless of the solvent used for IP.

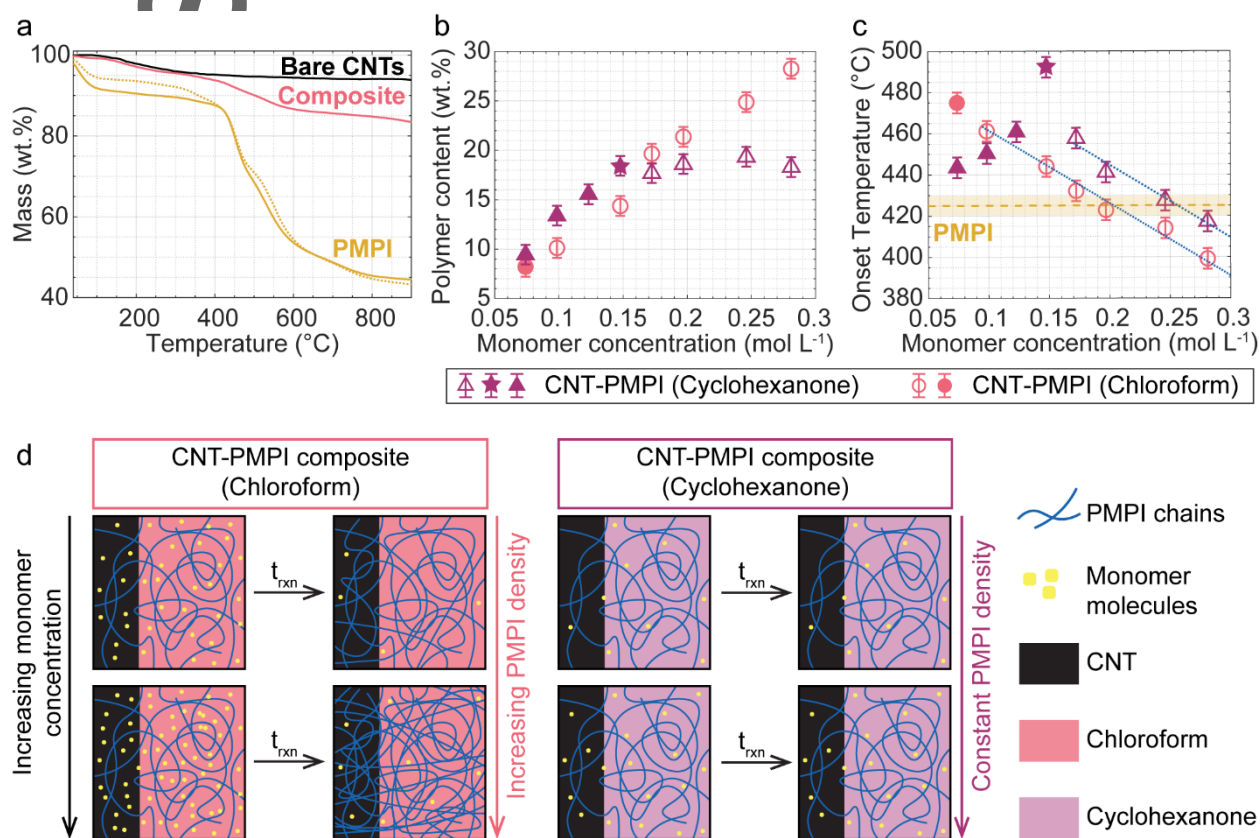
305 The varied evolution of polymer content with $[M]_0$ in the transport-limited regime can be
306 understood by comparing the solubility of PMPI in the two organic solvents, and its impact of the
307 final density of the polymer formed. In this analysis, we consider that the PMPI formed by ISIP is
308 amorphous, as observed by Transmission Electron Microscopy (TEM) (Figure 4b) and expected from
309 the high polydispersity which results from the IP reaction.^[27] We calculate the polymer-solvent
310 interaction parameter $\chi_{PMPI,solv}$ based on the Hildebrand solubility parameters for PMPI,
311 cyclohexanone, and chloroform following the formalism:^[14]

$$\chi_{PMPI,solv} = \frac{v(\delta_{PMPI} - \delta_{solv})^2}{RT}$$

312 Here v is the molar volume ($\text{m}^3 \text{mol}^{-1}$) of the solvent, δ_{PMPI} and δ_{solv} are the Hildebrand solubility
313 parameters ($\text{Pa}^{1/2}$) for PMPI and the solvent respectively, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the ideal gas
314 constant, and $T = 298 \text{ K}$ the temperature. We consider $\delta_{PMPI} = 26.8 \text{ MPa}^{1/2}$ as reported in the
315 literature^[28] and confirmed by Van Krevelen group contribution calculation for solubility parameters
316 and molar volumes.^[28] The values $\delta_{cyclo} = 19.6 \text{ MPa}^{1/2}$, $v_{cyclo} = 104 \text{ mL mol}^{-1}$, $\delta_{chloro} =$
317 $19.0 \text{ MPa}^{1/2}$, and $v_{chloro} = 80.7 \text{ mL mol}^{-1}$ for cyclohexanone and chloroform were taken from the
318 literature.^[28]

319 We find that $\chi_{PMPI,chloro} = 1.98$ and $\chi_{PMPI,cyclo} = 2.18$. This is in agreement with the experimental
320 observation that both chloroform and cyclohexanone are poor solvents for the polymer ($\chi > 0.5$),
321 and result in precipitation of PMPI upon polymerization. Nevertheless, chloroform is a better solvent

322 for the polymer (lower χ), suggesting that it can swell the solid PMPI forming at the surface of the
 323 CNTs to a greater extent, allowing for reactive monomer molecules to be trapped in the network
 324 (Figure 5d). We hypothesize that, with time, more polymer chains form from the trapped monomers
 325 and densify the solid PMPI coating attached to the CNTs, as this has been observed for multiple
 326 polyamide systems formed by traditional IP at a liquid-liquid interface.^[29] Cyclohexanone does not
 327 result in as much swelling of the polymer, and the mass density of the polymer stays constant,
 328 resulting in a stagnation of the polymer content with $[M]_0$.



329

330 **Figure 5.** Thermogravimetric analysis (TGA) of the CNT-PMPI composites. (a) Representative TGA
 331 decomposition profiles obtained for the bare CNT structure, the pure polymer, and the composite.
 332 The solid and dashed yellow lines correspond to PMPI synthesized by IP in the absence of CNTs in
 333 chloroform and cyclohexanone, respectively. (b) Evolution of the polymer content in the composite
 334 with monomer concentration. (c) Evolution of the decomposition temperature of the PMPI in the

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335 composite with monomer concentration. Filled markers correspond to the reaction-limited regime,
336 star-shaped markers to the uniformly-filled regime, and empty markers to the transport-limited
337 regime. The error bars represent the standard deviation of values obtained from analysis of three
338 samples in each polymerization condition. The average value of decomposition temperature (yellow
339 dashed line) for PMPI synthesized in the absence of CNTs, and standard deviation between samples
340 synthesized under the same conditions (yellow shaded area) are also plotted for comparison. (d)
341 Schematics explaining the qualitative evolution of PMPI density with monomer concentration,
342 depending on the organic solvent. t_{rxn} refers to the duration of the ISIP reaction.

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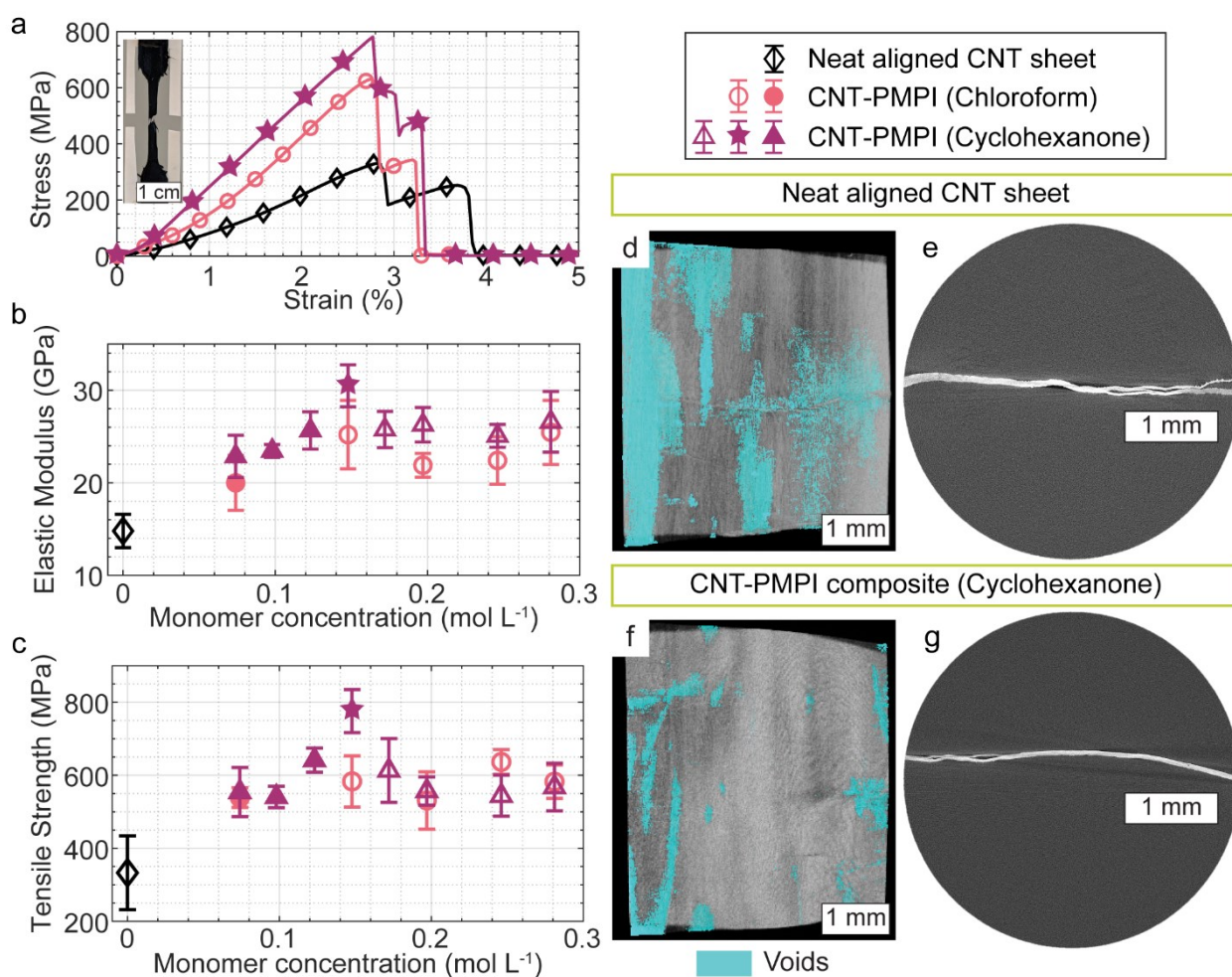
344 2.4. Mechanical properties and fracture mechanics

345 Mechanical properties also guide interpretation of the CNT-PMPI composite morphology, and the
346 role of homogeneity and polymer distribution at larger length scales. Uniaxial tensile testing was
347 performed on CNT-PMPI composite sheets obtained by ISIP (Figure 6). The composite samples were
348 cut into dog-bone specimens following the ISO-37 standard (Type 4 geometry) for tensile testing.
349 Load was applied along the alignment direction of the CNTs. Representative engineering stress-strain
350 curves for the bare aligned CNT sheet and the ISIP composites (Figure 6a) indicate a toe region
351 followed by a linear region. The toe region is attributed to the rearrangement of the CNTs, which
352 become more uniformly aligned along the loading direction with increasing strain. This is a
353 characteristic behavior of CNT assemblies^[30], as well as biological fiber-reinforced composites^[31] and
354 nanofiber mats.^[32] The maximum stress corresponds to the initial failure point in the gauge region.
355 Upon further loading, the specimen exhibits decreased stiffness but continues to carry load until
356 final failure. We observed that all specimens develop multiple local failures. This is commonly
357 observed for both CNT neat assemblies^[33] and composites,^[34] as well as carbon fiber composites^[35,36]
358 and is attributed to sequential failure CNT bundles and CNT-polymer interfaces, as well as
359 redistribution of stress as loading proceeds.

360 CNT-PMPI composites obtained with cyclohexanone in the uniformly-filled regime exhibit
361 significantly higher values of elastic modulus (Figure 6b) and tensile strength (Figure 6c) compared to
362 both the neat aligned CNT sheets and the CNT-PMPI composites obtained in the reaction-limited and
363 transport-limited regimes. The same trend is observed for specific modulus and specific strength
364 (Figure S4). Specifically, uniformly-filled CNT-PMPI composites exhibit an elastic modulus of 31 GPa
365 (22 N Tex^{-1}) and a tensile strength of 776 MPa (0.56 N Tex^{-1}); these values are 2.0- and 2.3-fold

366 greater, respectively, than the values for neat aligned CNT sheets. On the other hand, for both
367 chloroform and cyclohexanone, CNT-PMPI composites obtained in the reaction-limited and
368 transport-limited regime show values of elastic modulus and tensile strength of 24 GPa and 600
369 MPa.

370 While the above results show significant increases in both the absolute, and density-normalized
371 tensile properties, the modulus and strength of both the CNT networks and the composites are far
372 below expectations for highly-ordered, dense CNT materials.^[5] We attribute this difference to the
373 presence of voids in the starting CNT sheets, as confirmed by X-ray computed tomography (CT)
374 (Figure 6d-g). These voids result from the manufacturing technique used to form the CNT sheets. In
375 the floating catalyst CVD method, the CNTs form an aerogel-like “sock” which collapses prior to
376 mechanical collection from the furnace; this resulting CNT sheet is then aligned by wet-stretching^[22]
377 to form the CNT ribbons used as a starting material in this work. As the sock forms, it typically has a
378 highly entangled web of CNTs on the outer surface, and a low-density, low-entanglement core
379 where the carrier gas mainly flows.^[37] The invariance of the modulus and strength with $[M]_0$ in the
380 reaction-limited and transport-limited regime suggests that the flaws resulting from the CNT sheet
381 morphology cause preferential failure via internal stress concentration within the composite.



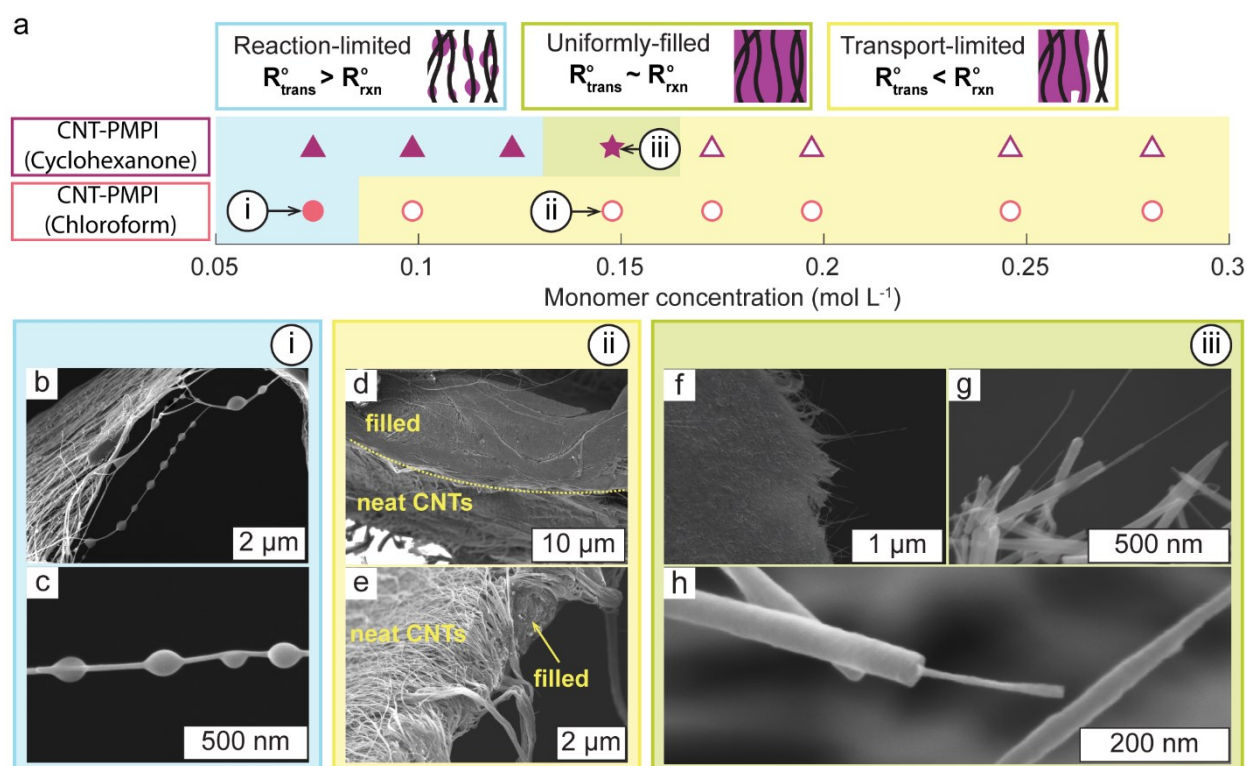
382
383

384 **Figure 6.** Mechanical properties of CNT-PMPI composite sheets. (a) Typical Stress-Strain curves for
 385 the bare CNT structure as well as the CNT-polymer composites. Inset: Dog-bone sample used for
 386 tensile testing. (b,c) Evolution of the (b) elastic modulus and (c) tensile strength with the monomer
 387 concentration. Filled markers correspond to the reaction-limited regime, star-shaped markers to the
 388 uniformly-filled regime, and empty markers to the transport-limited regime. The error bars
 389 represent the standard deviation of values obtained from analysis of between five and seven
 390 samples in each polymerization condition. (d-g) X-ray tomography reconstruction and representative
 391 slice of (d,e) a neat CNT sheet, and (f,g) a CNT-polymer composite obtained by ISIP for $[M]_0 = 0.15$
 392 mol L⁻¹ in cyclohexanone. The areas colored in blue in the reconstruction correspond to large voids
 393 (>5 μm).

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395 Therefore, we may rely on local observations of fracture mechanics as a more useful guide to the
396 role of polymer formed by ISIP on reinforcing the CNT network (Figure 7). SEM fractography provides
397 visual confirmation of which IP parameters result in the reaction-limited, uniformly-filled, and
398 transport-limited regimes (Figure 7a). At low monomer concentration ($[M]_o \leq 0.125 \text{ mol L}^{-1}$ for
399 cyclohexanone and $[M]_o \leq 0.075 \text{ mol L}^{-1}$ for chloroform), the fracture surface of the composite
400 reveals beads of PMPI adhered to CNTs (Figure 7b,c). At high monomer concentrations ($[M]_o \geq$
401 0.175 mol L^{-1} for cyclohexanone, and $[M]_o \geq 0.095 \text{ mol L}^{-1}$ for chloroform), the transport-limited
402 regime results in delamination at the interface between the polymer-rich outer region and the
403 polymer-depleted inner region (Figure 7d,e). In the uniformly-filled regime, fracture profiles show
404 crack propagation throughout the polymer-filled region and reveal CNTs surrounded with polymer
405 sheathings of various sizes (Figure 7f-h). The smooth cylindrical shape of the PMPI sheathing
406 suggests that ISIP results in a strong chemical interaction between PMPI and the CNTs (Figure 7h). To
407 the best of our knowledge, such polymer sheathing fracture morphology has only been observed in
408 the case of poly(vinyl alcohol)^[38] and polycarbonate^[39] in CNT composites obtained by polymer
409 solution infiltration. Notably, the uniformly-filled regime could only be resolved experimentally
410 when cyclohexanone was used as the organic solvent. Indeed, we observe that incrementing $d[M]_o$
411 of 0.025 mol L^{-1} in chloroform results in a jump from the reaction-limited to the transport-limited
412 regime, while in cyclohexanone the same increment corresponds to a transition from reaction-
413 limited to the uniformly-filled regime. This suggests that the range of concentrations $d[M]_{o,crit}$ at
414 which uniform polymer distribution can be obtained in chloroform is $< 0.025 \text{ mol L}^{-1}$, while it is $<$
415 0.05 mol L^{-1} in the case of cyclohexanone.



416

417 **Figure 7.** Fractography and nanoscale morphology. (a) Evolution of the morphology of the
 418 composites with monomer concentration and solvent type, showing three main regimes depending
 419 on the rate-limiting step, from a reaction-limited regime at low monomer concentration to a
 420 transport-limited regime at high monomer concentration. Filled markers correspond to the reaction-
 421 limited regime, star-shaped markers to the uniformly-filled regime, and empty markers to the
 422 transport-limited regime. (b-h) Corresponding fracture profiles for composites in each regime
 423 corresponding to data points (i), (ii), and (iii) as indicated in (a).

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426 **3. Discussion**

427 ISIP enables the creation of CNT-polymer composites with tailored polymer morphology and loading.
428 The rapid polymerization reaction could be scaled to a continuous process, as has been
429 demonstrated in the case of thin film composite (TFC) membranes for desalination technologies,
430 wherein thin polymer films are produced at liquid-liquid interfaces.^[18,40] Additionally, the process is
431 viable for any step-growth reactions and can be adapted to various polymer types such as
432 polyesters,^[41] polyureas,^[42] or polyimides,^[43] opening new range of accessible properties and
433 potential applications. The easily CNT-aramid composites described here feature improved
434 mechanical properties and high thermal stability, making them suitable candidates for applications
435 such as electromagnetic shielding.

436 Nevertheless, the rapid polycondensation reaction rate of ISIP results in a large polydispersity index
437 comparable to or greater than the Flory limit of 2. This high polydispersity makes the process
438 unsuitable to produce polymers with high crystallinity. Additionally, the window of processing
439 parameters to obtain a uniform composite may seem narrow, with only one tested concentration
440 resulting in such morphology in the current study. However, adjusting other processing parameters
441 such as pH of the aqueous phase, or the use of a solvent even more miscible in water such as
442 tetrahydrofuran (THF), could broaden the concentration range $d[M]_o^{crit}$ at which the uniformly-filled
443 morphology can be obtained. Additionally, finer control of the morphology and accurate prediction
444 of the processing windows can be achieved through a quantitative understanding of the interplay
445 between reaction kinetics and transport kinetics, as well as how the CNT surface and network
446 morphology influences polymer formation and adhesion.

447 Importantly, ISIP features shorter processing times than direct polymer infiltration and, to our
448 understanding, preserves the morphology of the CNT network. Improvements in the neat CNT sheet
449 morphology, as well as local microscale mechanical characterization would enable deeper
450 understanding of the CNT-polymer interaction and scaling of the mechanical properties to
451 structurally relevant levels. Finally, ISIP is not limited to CNT networks and could be used to obtain
452 composites of polymers and other porous materials such as electrospun nanofiber mats, or foams.

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455 **4. Conclusion**

456 We show that ISIP within a nanoporous CNT assembly enables the formation of CNT-aramid
457 composites, which cannot easily be obtained by polymer solution infiltration or melt processing due
458 to polyamide's insolubility in most organic solvents and high melting point. We demonstrated the
459 ability of ISIP to form CNT-polymer composites with tunable polymer loading, reaching full and
460 uniform loading under particular conditions guided by chemical kinetics theory. Tensile strength and
461 elastic modulus of the composites obtained by this method are superior to those of neat CNT
462 structures and could be improved by reducing voids already present in the starting CNT material. ISIP
463 shows potential for scale up as it not only could be applied to a wide variety of polymer systems (e.g.
464 polyamides, polyesters, polyimides), but it also features short processing times, and the potential to
465 be integrated in a roll-to-roll manufacturing process.

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466 **5. Experimental Section**

467 *Manufacturing and preparation of CNT sheets:* CNT sheets were manufactured by Nanocomp
468 Technologies, Inc using a floating catalyst CVD process. After synthesis, the CNT sheets are liquid-
469 saturated and stretched by ~35%, resulting in a final CNT Herman orientation factor of 0.7.^[22] The
470 sheets also have 5-10wt.% amorphous carbon and 10-20wt.% residual catalyst. Particular attention
471 was given to confirming the absence of carboxylic acid groups at the surface of the CNTs, as such
472 functionalities could react with the diamine monomer molecules and result in covalent bonding of
473 the polymer chains with the CNTs. First, elemental analysis (EDS) on neat CNT sheets reveal only a
474 residual amount of oxygen (3.9 at.%, Table S2) which is attributed to defects at the surface of the
475 CNTs from the CVD growth process and the presence of residual iron oxide catalyst particles.
476 Moreover, Raman spectroscopy (Figure S5) reveals CNTs with low defect density (ID/IG ratio of 0.33)
477 and TGA in air (Figure S6) shows no significant mass loss at 300°C, which is the expected
478 decomposition of carboxylic groups.^[44] For each ISIP experiment, pieces of the CNT sheet were
479 mounted on the sample carousel and immersed in deionized water for 30 minutes before any
480 immersion in monomer solutions.

481 *Interfacial polymerization:* All chemicals were used as received and did not undergo any additional
482 purification. Isophthaloyl Chloride ($\geq 99\%$) was obtained from TCI America and stored under inert
483 atmosphere to prevent hydrolysis of the compound. M-phenylene diamine ($\geq 99\%$) was purchased
484 from Millipore Sigma and was also stored under inert atmosphere. Chloroform (containing 100-200
485 ppm amylenes as stabilizer, $\geq 99.5\%$), cyclohexanone (ACS reagent, $\geq 99.0\%$), water (ACS reagent),
486 and acetone (ACS reagent, $\geq 99.5\%$) were also obtained from Millipore Sigma. Glassware was always
487 rinsed twice with the solvent that it would contain prior to solution preparation or to the

488 polymerization reaction. Monomer solutions were prepared by weighing the monomers and
489 dissolving them in their respective solvents (diamine in water and acyl chloride in organic solvent) in
490 a conical flask equipped with a magnetic stir bar. The volume of solvent was measured with a
491 graduated cylinder. Monomer concentration in mol.L⁻¹ was the same for both solutions to maintain a
492 1:1 molar ratio between the diamine and acid chloride. Aqueous solutions were prepared and stored
493 in amber glassware to prevent damage of the diamine monomer which features UV sensitivity.

494 For ISIP a custom-made experimental setup (Figure S7) was developed in order to produce CNT-
495 polymer composites at high throughput. A sample carousel which could hold and rotate six CNT
496 ribbons at once was designed to rotate the samples in the sequential solutions, and machined out of
497 chemically resistant materials (Aluminum 6061, 316 Stainless Steel, and Kalrez® rubber) (Figure S7a-
498 c). The carousel attachment consisted of an aluminum plate with six radial slots and a set screw to
499 fix each sample in place with regard to the disk (Figure S7a). Each CNT sample was kept under light
500 tension by a set of custom-made clamps, mounted on a shaft and equipped with Kalrez® rubber to
501 hold the CNT assemblies without damaging it (Figure S7b). The carousel assembly was held by a
502 rotary shaft fixed with regard to the aluminum disk, and fits in a spinner flask featuring two 45°
503 necks which were used for liquid addition or removal (Figure S7c). The spinner flask was sealed with
504 a cap equipped with a gasket which prevented solvent evaporation while allowing carousel rotation
505 inside the subsequent solvent baths at a speed of approximately 50 rpm. The experimental setup
506 described above was used in a multiple step process to obtain CNT-PMPI composites by ISIP. The
507 neat CNT assemblies were first immersed in an aqueous solution of m-phenylene diamine (0.075-
508 0.28 mol.L⁻¹) for 20 minutes to ensure complete wetting of the network. The excess solution was
509 shaken off the clamp and the outer surface of the sample by increasing the speed of the carousel to

510 150 rpm for 2 seconds. This allowed the aqueous phase to be retained within the network without
511 having a film of water on the outside of the sample which could react with the organic phase and
512 prevent the transport of the organic solvent inside the pores of the CNT assembly. The ribbons were
513 then immersed in an organic solution of isophthaloyl chloride (1:1 molar ratio with m-phenylene
514 diamine to preserve stoichiometry of the reaction) dissolved in chloroform or cyclohexanone. The
515 reaction was left to proceed for 5 minutes before the resulting composite was transferred first to a
516 DI water rinsing bath (to wash off the by-product) and second to an acetone rinsing solution (to
517 wash off the unreacted monomers). Finally, the CNT ribbons were removed from the clamps and left
518 to dry in air overnight.

519 To obtain the decomposition temperature of pure PMPI, we conducted IP at the liquid-liquid
520 interface in a classical beaker setup, in absence of CNTs.^[15] In this case, 100 mL of both solutions
521 were used. In the case of chloroform, the chloroform solution was poured into the beaker first due
522 to its greater density than water. In the case of cyclohexanone, the aqueous phase was denser and
523 was at the bottom of the beaker, while the organic phase rested on top of the water phase. An
524 aramid film formed at the interface between the two liquids immediately. As PMPI is an aromatic
525 polyamide, the polymer chains act as rigid rods and do not feature enough entanglement to pull the
526 film as a continuous rope from the liquid-liquid interface as it is commonly done for aliphatic
527 polyamides. From this perspective, the beaker was equipped with a custom-made polymer film
528 collector consisting of a 316 stainless steel mesh, supporting a circle of filter paper. Both the mesh
529 and the filter paper had the same diameter as the beaker to maximize the amount of polymer film
530 collected by this method. The polymer film collector was set to rest at the bottom of the beaker
531 before the monomer solutions were poured into the reaction vessel. The mesh featured two handle

532 accessible from the top of the beaker allowing to lift the collecting device up and collect the polymer
533 film formed at the interface between the two liquids. After a reaction time of 5 minutes, the top
534 phase was removed with a custom-made glass siphon and the polymer film was collected onto the
535 filter paper by lifting up the polymer film collector. The polymer was scraped off the filter paper,
536 rinsed twice in both water and acetone, and isolated by filtration.

537 *Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy:* SEM images were obtained
538 with a Zeiss Merlin High-Resolution Scanning Electron Microscope (SEM) using the High Resolution
539 mode, the in-lens detector, an acceleration voltage of 3kV, and a probe current of 100 pA. To obtain
540 qualitative information about the elemental distribution throughout the thickness of the
541 composites, Energy-Dispersive X-ray Spectroscopy (EDS) was conducted using an EDS detector and
542 the software APEX. A line profile across the thickness of the samples, a working distance of 10 mm, a
543 linewidth of 1 μm , an integration time of 100 ms and 16 frames were used to allow for the detection
544 of low-atomic-number elements. In the case of EDS measurements, the acceleration voltage was
545 increased to 10kV and the probe current to 500 pA. Considering the challenges associated with
546 measuring small atomic number elements by EDS, we compared the average nitrogen content to the
547 nitrogen at.% calculated from TGA measurements of the polymer content. In all cases, the average
548 at.% nitrogen measured by EDS was within the error bars of the expected value obtained from
549 thermal analysis, confirming that the signal actually emerged from PMPI (Figure 3b, c).

550 *Transmission electron microscopy and associated sample preparation:* Thin lamellae for TEM images
551 were prepared by two methods. A first set of lamellae was prepared by Cryo-FIB on a Zeiss
552 Crossbeam 540 Scanning Electron Microscope, to prevent damaging the polymer or CNTs by the ion
553 beam. H-shaped lamellae were obtained by milling normally to the composite cross sections (parallel

554 to the CNT alignment direction). Microtome sectioning was also used to prepare 60-nm thick TEM
555 lamellae by cutting normal to the CNT alignment direction. Prior to microtoming, small sections (~1.5
556 mm) of the CNT-PMPI composites were embedded in EMBED 812 according to a multi-step
557 procedure. First, the specimens were placed in a vial and immersed in 200 proof EM grade ethanol
558 overnight, followed by soaking in a 50:50 mixture of ethanol and embedding resin for two days. In
559 both of those stages, the vial was kept in a tube rotator to ensure agitation of the liquid medium.
560 Second, the soaked samples were laid out in a flat silicone embedding mold, covered by a thin layer
561 of resin, and cured at 60°C for one day. After curing, the samples were flipped over in the
562 embedding mold and a layer of fresh resin was poured on top, followed by curing in the same
563 conditions. This two-step embedding process ensures centering of the CNT composite within the
564 resin. Microtoming was performed with a histology diamond knife at room temperature on a Leica
565 Ultracut UCT. TEM was performed on both a high resolution JEOL 2100F TEM and a Hitachi 7800
566 TEM.

567 *Thermogravimetric analysis:* Thermogravimetric analysis (TGA) was performed on a TA instrument
568 Discovery TGA. The sample was cut in small pieces and a mass of approximately 1 mg was put into a
569 Platinum HT pan. The temperature was ramped up from 40°C to 900°C at a heating rate of 10°C min⁻¹
570 in Nitrogen. The TGA data was then analyzed using TA instrument software TRIOS to find the onset
571 temperature and polymer content. For the different monomer concentrations and solvents, we
572 calculated the polymer content and onset temperature in accordance with ASTM® E2550 – 17
573 standard. Three samples synthesized in the same conditions were tested by TGA to obtain the
574 standard deviation on the onset temperature and polymer content.

575 *Uniaxial tensile testing:* The CNT ribbons were cut with a stainless steel scalpel into dog-bone
576 specimens following ISO- 37 standard (Type 4 geometry) prior to being tested. The cut was
577 performed using an acrylic mask which featured a path where the scalpel could be inserted to cut
578 the CNT ribbon pressed between the acrylic mask and a cutting mat. Uniaxial tensile testing was
579 performed at a strain rate of 3mm min^{-1} on an Instron 8848 MicroTester equipped with a 50 N load
580 cell. Five to seven samples synthesized in the same conditions were mechanically tested to obtain
581 values of elastic modulus and tensile strength as well as the standard deviation.

582 *X-ray tomography:* X-ray tomography was performed on a Zeiss Versa 520 machine, adjusting the
583 source and detector distances to obtain a voxel size of $2\ \mu\text{m}$. The sample was clamped with the long
584 axis of the ribbon pointing in the vertical direction. Rotation axis corresponded to the long axis of the
585 ribbon (alignment direction of the CNTs). Data acquisition was controlled with the software Scout-
586 and-Scan™ Control System. A 3D image was generated from the individual slices using the software
587 Dragonfly 4.1.

588

589 **Supporting Information**

590 Supporting Information is available from the Wiley Online Library or from the author.

591

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607

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666 **Keywords**

667 carbon nanotubes, polymerization, interface, composites, mechanics

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671 **Title**

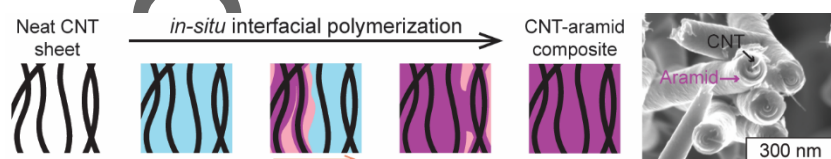
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673 **Carbon Nanotube-Polymer Composites.**

674 Cécile A. C. Chazot, Carolyn K. Jons, and A. John Hart*

675

676 **TOC figure**

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