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High strength metakaolin-based geopolymer reinforced by pristine and covalent functionalized carbon nanotubes

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35 **1. Introduction**

36 Developing a higher-strength geopolymer material is a great challenge in civil engineering,
37 offering a new generation of building and construction materials with better mechanical
38 properties, lower shrinkage and superior durability as well as environmental sustainability. A
39 promising way to achieve this development is the incorporation of nanomaterials, which
40 minimizes the air gaps content in the nanostructure and allows for a non-corrosive
41 reinforcement. The denser microstructure positively affects the physical and mechanical
42 properties of the novel nanocomposite. Researchers attempt to incorporate different
43 nanofillers to enhance the performance of geopolymer materials. Xie and Fang¹, and Sumesh
44 et al.² reviewed the modification of geopolymer composites properties with nanomaterials and
45 underline that most attention was paid to the influence of nano-SiO₂, nano-Al₂O₃, nano-TiO₂,
46 nano-Fe₂O₃, and nano-clay. Experimental SEM tests reveal that the addition of 6% of nano-
47 SiO₂ leads to the improvement in compressive, flexural and tensile strength at 28 days under
48 ambient temperature curing³. The work of Phoo-ngernkham et al.² shows that the
49 incorporation of 2% of nano-silica and 1% of nano-alumina cured for 90 days, gives the
50 compressive strength of 51.8 and 56.4 MPa, respectively⁴. Of late years, research on the
51 addition of carbon-based nanomaterials in geopolymers has drawn research attentions⁵⁻¹⁰.
52 Particularly, carbon nanotubes (CNT's) are expected to be excellent candidates and
53 innovative reinforcements due to their superior mechanical properties¹¹. However, the main
54 prerequisites that determine the performance of the CNT/geopolymer are the good
55 dispersion¹²⁻¹⁵. In fact, due to the highly attractive van der Waals forces, CNT tend to remain
56 agglomerated, which causes the decrease of the performance of composites¹⁶⁻¹⁹. To date,
57 extensive research is made on the study of the mechanical enhancement of CNT on
58 geopolymer. Abbasi et al.¹⁴ reported that the addition of only 0.5 wt% Multi-Walls CNT
59 (MWCNT) on fly ash leads an increase of flexural strength and elastic modulus by 128% and
60 109%, respectively. On the other hand, the experimental work of Saafi et al.¹⁹ showed that the
61 addition of MWCNTs increased the flexural strength, Young's modulus and flexural
62 toughness by 160%, 109% and 275%, respectively. It also enhanced the fracture energy and
63 increased the electrical conductivity by 194%. Luz et al.²⁰ observed that the addition of 0.1
64 wt% of pristine CNT in metakaolin geopolymer leads improvements of 3.8%, 13.2% and
65 28.7% in the Young's modulus, compressive and flexural strengths, respectively.
66 Nevertheless, an increase of about 10.2% in the porosity is obtained when the dosage of CNT
67 exceeds 0.2 wt% inducing to a decrease of 3.5%, 11.8% and 31.0%, for Young modulus,
68 compressive and flexural strengths, respectively. Yuan et al.²¹ reported that 3 wt% of COOH-

69 multi-walled CNT enhances the flexural strength, the elastic modulus and the fracture
70 toughness within 42.3%, 29.6% and 38.5%, respectively. Moreover, it is found that the
71 inclusion of graphene and its derivatives such as graphene oxide and reduced graphene oxide
72 lead to interesting properties²². Zhang et al.²³ studied the substitutional doping of graphene
73 with silicon incorporated in metakaolin geopolymer using reactive molecular dynamics
74 simulations. Their obtained results show that the elastic modulus of 10% Si-
75 graphene/geopolymer is double than graphene/geopolymer matrix. Besides, the dispersion
76 problem encountered during the CNT reinforcement and interfacial chemical bonding have
77 also a great impact on the structure and mechanical properties of the reinforced
78 nanocomposite, as reported in some works²⁴⁻²⁵.

79 Though all research is promising, more efforts are deemed necessary essentially in modeling
80 and simulation to bridge the gaps with experimental findings. Only two works have been done
81 on atomistic simulation of the reinforcement of geopolymers through the incorporation of
82 carbon-based materials^{23, 26}. In these two studies^{23, 26}, authors fixed the concentration of Si-
83 doped graphene and CNT to be around 6 wt%. According to all experimental measurements³⁻
84²¹ performed in that subject, the dosage of incorporated nanomaterials is of great importance
85 and affects considerably the mechanical properties of reinforced geopolymers. Therefore the
86 main novelty of this work compared to previous studies^{23,26} is that we consider for the first
87 time the incorporation of CNT nanofillers with a dosage varying from 0 to 8.31 wt%. We will
88 focus on elucidating the effect of pristine and covalent functionalized CNT on the mechanical
89 properties of metakaolin geopolymer. Based on molecular dynamics simulation and using a
90 reactive force field, we aim mainly to find the optimum dosage for CNT that enhances the
91 elastic response of CNT/geopolymer nanocomposite. Moreover, the role of functionalized
92 CNT on the improvement of their mobility and the stability of the nanostructure is also
93 discussed.

94

95 **2. Molecular modeling and force fields**

96 According to Davidovids^{27, 28}, creating geopolymer paste requires alumina silicate material
97 (metakaolin, fly ash, etc.), alkaline reagent (sodium or potassium soluble) and water. In the
98 first step of polymerization, the dissolution of aluminosilicate source in the alkali solution
99 leads to the formation of Al-OH and Si-OH bonds²⁹. After the hydrolysis process, Al(OH)₄
100 and Si(OH)₄ are released and then polymerized to form aluminosilicate oligomers³⁰⁻³¹. Finally
101 the condensation reactions produce a crosslinked 3D network structure from which we can
102 class mainly three types of structures depending on Si/Al ratio: sialate (Si/Al = 1), sialate-

103 siloxo (Si/Al=2), and sialate-disiloxo (Si/Al = 3). In the present study, we use sialate-disiloxo
 104 oligomers (Si/Al = 3) (NaAlSi₃O₁₃) to represent the geopolymer structure. The preparation of
 105 CNT/geopolymer model evolves the following steps: first a supercell with a size of 8x 8 x 8
 106 nm is built where (6,6) CNT molecules with various concentrations (0 – 8.31 wt%) are
 107 dispersed randomly. Then 1601 oligomers are packed into the box within water molecules so
 108 that the water content in the nanostructure is fixed to 7.7 wt.%, as reported in the work of
 109 Zhang et al.³². The density of the system is equal to 2 g/cm³ leading to a model nanostructure
 110 of 38361 atoms. The chemical composition of metakaolin geopolymer model is presented in
 111 Table 1. A side view the CNT/geopolymer model with 3.73 wt% CNT concentration is
 112 presented in Fig.1. In the present study, pristine and CNT-oxide molecules are used within
 113 various hydroxyl groups attached to randomly carbon atoms, as presented in Fig.2. The CNT-
 114 oxide concentrations are equal to 0% (pristine CNT), 2.5%, 5%, 7.5% and 10% (Fig.2b).
 115 In this study, Reactive force field (ReaxFF), developed by van Duin et al.³³ is carried out to
 116 represent the interatomic interactions in the CNT/geopolymer model. It is a bond-order
 117 dependent potential where the atomic charges are calculated from its charge equilibration
 118 nature, which makes it possible to simulate chemical reactions. The bond order is directly
 119 calculated from the instantaneous distances that are updated systematically allowing the
 120 creation and dissociation of bonds during simulation. The total energy (E_{Tot}) of a system, as
 121 described in equation (1), is of a sum of several energies: the bond formation energy (□□□□),
 122 the van der Waals energy (□□□□), the Coulombic contribution (□□□□), the angular and
 123 torsional energy (□□□□, □□□□), the lone pair energy (□_{lp}) and finally the energy penalty for
 124 under/over coordination stability of atoms (□□□□□□, □□□□□□):

125

$$126 \quad E_{\text{Tot}} = E_{\text{bond}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{angular}} + E_{\text{torsional}} + E_{\text{lp}} + E_{\text{coordination}} + E_{\text{other}}$$

127 (1)

128

129 The ReaxFF forcefield has been applied successfully on geopolymer²³, calcium silicate
 130 hydrates³⁴, sodium aluminosilicate glass^{35,36}, silica^{37,38}, zeolite^{39,40} and clay minerals^{41,42}.

131

132 3. Simulation procedure

133 The CNT/geopolymer model, as presented in section II, is first relaxed based on the conjugate
 134 gradient algorithm with a convergence criterion of 10⁻¹² kcal/mol to optimize the system
 135 geometry. Then molecular dynamics simulations are performed to equilibrate the system
 136 under an NVT ensemble for 100 ps at 300 K using a time step of 0.2 fs. After, a heating is

137 applied up to 2000K for 100 ps using a timestep of 0.2fs in NPT ensemble, followed by
138 quenching to 300K with a cooling rate of 1 K/ps to realize the polymerization of oligomer and
139 thus produce a cross-linked geopolymer matrix. The obtained structure is then relaxed in the
140 *NPT* ensemble for 200 ps at 300K. Periodic boundary conditions are applied to all directions
141 during the simulation procedure. Further equilibration for 1ns is performed to compute the
142 trajectory information of atoms in order to study the dynamical properties of the
143 nanostructure. A constant strain method is employed to calculate the mechanical properties
144 where a series of expansions at 0.0001/ps are applied to the supercell.

145

146 **4. Results and discussion**

147 *4. 1. Effect of pristine CNT content on the mechanical properties of geopolymer*

148 *nanocomposite*

149 Since their discovery, carbon nanotubes have aroused the interest of researchers as composite
150 reinforcements and weight reducers thanks to their high elastic modulus of $\sim 1 \text{ TPa}^{43}$. The
151 main concern of this section is to address the role of pristine CNT in reinforcing the
152 geopolymer nanostructure. The tensile processes are investigated by using the constant-strain
153 method to assess the elastic and indentation modulus of the CNT/geopolymer nanocomposites
154 with various CNT concentrations from 0.0 to 8.31 wt%. First, the obtained elastic modulus for
155 plain geopolymer model is found to be equal to 46.21 GPa, in agreement with the obtained
156 values of 45.1 GPa²³ and 42 GPa⁴⁴. Figures 3 and 4 depict the obtained data of the elastic and
157 the indentation modulus for various CNT concentrations. The data in Fig. 4 are compared to
158 experimental measurements⁴⁵ for only low CNT content and seems to be in agreement with
159 our results. It is noticed for both figures that the highest mechanical improvement is achieved
160 at CNT concentration of 1.08 wt%, with the elastic and indentation modulus increase of 74%
161 and 93.4%, respectively. Higher CNT dosage leads to a gradually strength decrease, due to
162 the highly attractive van der Waals forces between CNT caused by the high specific surface
163 area of CNT. This phenomenon will lead to the agglomeration of CNT, which makes the
164 dispersion problematic since it causes and a decrease of bonding between geopolymer and
165 CNT and hence affects the strength and the mechanical performance of the system. Using a
166 multi-stage hierarchical micromechanical model Hasanzadeh et al.⁴⁶ show that the CNT
167 agglomeration influences and degrades considerably the creep resistance of the CNT-polymer
168 system. It is also found that the interphase region affects mainly the effective properties of the
169 piezoelectric hybrid composites⁴⁷.

170 Besides, it is observed particularly that the addition of 8.31 wt% of CNT results to an elastic
171 modulus value of 45.59 GPa close to the value for the plain geopolymer (46.21 GPa). Our
172 results are in agreement with experimental work of Jittabut et al.⁴⁸ on reinforcing ash fly
173 geopolymer using CNT dosage from 1 to 5 % by weight. They found that the optimum of 1
174 wt% carbon nanotubes addition exhibited the highest strength increase (32%). Saafi et al.¹⁹
175 studied the effect of multiwalled carbon nanotubes (MWCNT) on fly ash geopolymeric
176 composites with very low concentrations (0.1%, 0.5%, 1%). Their experimental results
177 showed the enhancement of flexural strength, flexural toughness and Young's modulus is
178 128%, 207% and 109%, respectively at 0.5 wt% CNT content. On the other hand, Abbasi et
179 al.¹⁴ found that the addition of 0.5 wt% MWCNT increases the Young modulus and the
180 flexural strength by 109% and 128%, respectively.

181 The bulk densities of CNT/geopolymer nanostructure are calculated for various CNT
182 concentrations, as shown in Fig.5. The results follow the same tendency as for the mechanical
183 findings since an optimum value of the bulk density is obtained for the sample with 1.08 wt%
184 of CNT addition. For higher concentrations, the bulk densities values decrease but they
185 remain higher than the plain geopolymer's data. The study of the interfacial energy variation
186 with CNT content, as presented in Fig.6, proves the stability of the nanostructure at 1.08 wt%
187 concentration since the obtained energy is the lowest one. Therefore, it can be seen that the
188 incorporation of low content of pristine CNT has a beneficial effect on condensing the
189 metakaolin geopolymer nanocomposite and enhancing the corresponding mechanical
190 properties.

191

192 *4.2. Effect of functionalized CNT*

193 Our results as well as experimental studies^{14, 20} show a strength loss when CNT concentration
194 surpasses an optimum amount. This behavior is due to the agglomeration of CNT leading a
195 difficulty in uniformly dispersing CNT in geopolymer matrix. Luz et al.²⁰ reported that no
196 threshold was observed for functionalized CNT compared to pristine CNT. In this section our
197 aim is to study the variation of structural and elastic properties with covalent functionalized
198 CNT concentrations. As presented in Fig.2b, CNT-oxide molecules are used within hydroxyl
199 groups attached to randomly carbon atoms. The CNT-oxide doping concentrations are equal
200 to 2.5%, 5%, 7.5% and 10%. This functional group improves CNT dispersion and provides a
201 larger number of active sites for connection with geopolymer matrix. First, we address in Fig.
202 7 the variation of Elastic modulus of carbon nanotubes with OH concentrations. Compared
203 with pristine CNT, CNT-oxide has lower elastic modulus since covalent bonds created

204 through C-OH interaction lead to defects creation converting their surface SP² hybridation to
205 SP³⁴⁹⁻⁵¹. At OH concentration of 10%, CNT-oxide loose about 25% in the elastic modulus.
206 Zhang et al.²³ reported also that the graphene oxide and Si-graphene (doping concentration of
207 10%,) show losses in the elastic modulus of about 9.9 and 43.3%, respectively. However, as
208 the elastic properties of Si-graphene and in our case CNT-oxide are much higher than that of
209 geopolymer structure, they found that such nanofillers possess a great potential to reinforce
210 geopolymer composite.

211 In the following, calculations have been carried out in a supercell with a size of 3.5 x 3.5 x 5.5
212 nm containing one (6,6) CNT-oxide representing 6 wt% of CNT content in the nanostructure
213 (Fig.8). We have chosen this value in order to compare our results with those of Zhang et al.²³
214 using graphene oxide and Si-doped graphene with a concentration of about 6 wt%. Fig. 9
215 represents the variation of the mean and the transversal elastic modulus data with OH
216 concentrations, compared to the reactive molecular dynamics calculations of Zhang et al.²³. It
217 is observed that the mean young modulus increases with increasing C-OH concentration. The
218 obtained value at 10% C-OH is 2.65 times higher than the one obtained in the case of pristine
219 CNT due to the chemically bonded interface. The main enhancement comes from the
220 transversal elastic response of the nanostructure, as appeared in Fig.9. Moreover, one may
221 observe that incorporating CNT-oxide (with 10% C-OH concentration) into geopolymer
222 structure leads to a higher enhancement of the elastic modulus (165%) comparing to 65% in
223 the case of 10% Si-doping graphene²³. Moreover, it is found that the addition of 10% Si-
224 graphene²³, Young's modulus is enhanced by 64.2%. Fig. 10 illustrates the increase of the
225 bulk density of CNT-oxide/geopolymer with C-OH concentration. That means that the
226 nanostructure becomes denser for higher OH concentrations since the obtained raise is of
227 22.5% at 10% C-OH concentration.

228

229 4.3. Diffusion of CNT in geopolymer nanocomposites

230 With the aim of understanding the mobility of CNT in geopolymer matrix, we study in this
231 section the effect of covalent functionalization of CNT (10% C-OH) on the dynamical
232 properties of the nanostructure. Mean square displacement (*MSD*) and self-diffusion
233 coefficient (*D*) are analyzed for CNT atoms and Na⁺ cations for comparison, as presented in
234 the following equations:

235

$$236 \text{MSD}(t) = \langle |r_i(t) - r_i(0)|^2 \rangle \quad (2)$$

237

238
$$D = \frac{1}{6} \frac{MSD(t)}{t}$$

239

240 where $r_i(t)$ is the position of atom i at time t . As shown in Fig.11, MSD of CNT atoms and
241 Na^+ cations are higher in the case of functionalized CNT incorporation. The obtained
242 diffusion coefficients from the calculated slope according to equation (2) are reported in
243 Table 2, in comparison with previous theoretical calculations²⁶. The diffusion coefficient of
244 CNT-oxide is found to be three times higher than the one of pristine CNT. This diffusive
245 behavior of CNT-oxide is seen clearly in Fig.11a where a higher slope is observed. Besides,
246 our results show that the mobility of Na^+ cations is equal to $0.376 \times 10^{-11} \text{m}^2/\text{s}$ in the case of
247 the addition of pristine CNT to geopolymer matrix, in agreement with the calculated value of
248 $0.345 \times 10^{-11} \text{m}^2/\text{s}$ ²⁶. The functionalization of CNT leads to a rise of the diffusion of Na^+ cations
249 by a factor of 3 since the obtained value is equal to $1.113 \times 10^{-11} \text{m}^2/\text{s}$.

250

251 **5. Conclusion**

252 The present work addresses the subject of the improvement of the mechanical properties of
253 metakaolin geopolymer structure through the incorporation of CNT nanofillers with a dosage
254 varying from 0 to 8.31 wt%. By means of reactive molecular dynamics simulation, our results
255 demonstrates the presence of an optimum amount of pristine CNT (1.08 wt%) that enhance
256 the elastic and the indentation modulus up to 74% and 94%, respectively. Tensile tests show
257 that 10% doped CNT-oxide leads to a raise of the elastic modulus by 165% and makes the
258 structure denser. Finally, it is observed that functionalized CNT improves the mobility of
259 CNT in the matrix and makes the structure of geopolymer denser.

260

261

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270 **References:**

271 ¹ T.Y. Xie, C.F. Fang, Nanomaterials applied in modifications of geopolymer composites: a
272 review, *Aust. J. Civil Eng.* 17 (2019) 32–49.

273 ² M. Sumesh, U.J. Alengaram, M.Z. Jumaat, K.H. Mo, M.F. Alnahhal, Incorporation of nano-
274 materials in cement composite and geopolymer based paste and mortar – a review, *Constr.*
275 *Build. Mater.* 148 (2017) 62–84.

276 ³ D. Adak, M. Sarkar, S. Mandal, *Constr. Build. Mater.* 70 (2014) 453–459.

277 ⁴ P. Chindaprasirt, P. De Silva, K. Sagoe-Crentsil, S. Hanjitsuwan, s, *J. Mater. Sci.* 47 (2012)
278 4876–4883.

279 ⁵ S.J. Chen, F.G. Collins, A.J.N. Macleod, Z. Pan, W.H. Duan, C.M. Wang, Carbon
280 nanotube–cement composites: a retrospect, *ISE J. Part A: Civil Struct. Eng.* 4 (2011) 254–
281 265.

282 ⁶ H.B. Yang, H.Z. Cui, W.C. Tang, Z.J. Li, N.X. Han, F. Xing, A critical review on research
283 progress of graphene/cement based composites, *Compos. Part A Appl. S.* 102 (2017) 273–296.

284 ⁷ Y.D. Xu, J.Q. Zeng, W. Chen, R.Y. Jin, B. Li, Z.H. Pan, A holistic review of cement
285 composites reinforced with graphene oxide, *Constr. Build. Mater.* 171 (2018) 291–302.

286 ⁸ E. Shamsaei, F.B.D. Souza, X.P. Yao, E. Benhelal, A. Akbari, W.H. Duan, Graphene-based
287 nanosheets for stronger and more durable concrete: a review, *Constr. Build. Mater.* 183
288 (2018) 642–660.

289 ⁹ B.G. Han, S.Q. Ding, J.L. Wang, J.P. Ou, *Nano-Engineered Cementitious Composites:*
290 *Principles and Practices*, Springer, 2019.

291 ¹⁰ T.X. Huang, Z.Q. Sun, *Advances in multifunctional graphene-geopolymer composite,*
292 *Constr. Build. Mater.*, under review.

293 ¹¹ N.J. Coleman, U. Khan, W.J. Blau, Y.K. Gun-ko, Small but strong: a review of the
294 mechanical properties of carbon nanotube-polymer composites, *Carbon* 44 (2006) 1624–
295 1652.

296 ¹² G.M. Kim, I.W. Nam, B. Yang, H.N. Yoon, H.K. Lee, S. Park, Carbon nanotube (CNT)
297 incorporated cementitious composites for functional construction materials: the state of the
298 art, *Compos. Struct.* 227 (2019) 111244.

299 ¹³ H.M. Khater, H.A. Abd El Gawaad, Characterization of alkali activated geopolymer mortar
300 doped with MWCNT, *Constr. Build. Mater.* 102 (2016) 329–337.

301 ¹⁴ S.M. Abbasi, H. Ahmadi, G. Khalaj, B. Ghasemi, Microstructure and mechanical properties
302 of a metakaolinite-based geopolymer nanocomposite reinforced with carbon nanotubes,
303 *Ceram. Int.* 42 (2016) 15171–15176.

304 ¹⁵ K.J.D. MacKenzie, M.J. Bolton, Electrical and mechanical properties of aluminosilicate

305 inorganic polymer composites with carbon nanotubes, *J. Mater. Sci.* 44 (2009) 2851–2857.

306 ¹⁶ E.T. Thostenson, Z. Ren, T.-W. Chou, Advances in the science and technology of carbon
307 nanotubes and their composites: a review, *Compos. Sci. Technol.* 61 (2001) 1899–1912.

308 ¹⁷ F. Sanchez, K. Sobolev, Nanotechnology in concrete—a review, *Constr. Build. Mater.* 24
309 (2010) 2060–2071.

310 ¹⁸ P.M. Ajayan, L.S. Schadler, P.V. Braun, *Nanocomposite Science and Technology*, John
311 Wiley & Sons, 2006.

312 ¹⁹ M. Saafi, K. Andrew, P.L. Tang, D. McGhon, S. Taylor, M. Rahman, S.T. Yang, X. M.
313 Zhou, Multifunctional properties of carbon nanotube/fly ash geopolymeric nanocomposites,
314 *Constr. Build. Mater.* 49 (2013) 46–55.

315 ²⁰ G. Luz, P.J.P. Gleize, E.R. Batiston, F. Pelisser, Effect of pristine and functionalized carbon
316 nanotubes on microstructural, rheological, and mechanical behaviors of metakaolin-based
317 geopolymer, *Cem. Concr. Comp.* 104 (2019) 103332.

318 ²¹ J.K. Yuan, P.G. He, D.C. Jia, S. Fu, Y. Zhang, X.Z. Liu, D.L. Cai, Z.H. Yang, X.M.
319 Duan, S.J. Wang, Y. Zhou, In situ processing of MWCNTs/leucite composites through
320 geopolymer precursor, *J. Eur. Ceram. Soc.* 37 (2017) 2219–2226.

321 ²² Q. Zheng, B. Han, X. Cui, X. Yu, J. Ou, Graphene-engineered cementitious composites:
322 Small makes a big impact, *Nanomater. Nanotechnol.* 7 (2017) 1–18,
323 <https://doi.org/10.1177/1847980417742304>.

324 ²³ L.W. Zhang, M.F. Kai, X.H. Chen, Si-doped graphene in geopolymer: Its interfacial
325 chemical bonding, structure evolution and ultrastrong reinforcing ability, *Cem. Concr.*
326 *Compos.* 109 (2020), 103522, <https://doi.org/10.1016/j.cemconcomp.2020.103522>.

327 ²⁴ J. Lu, M. Luo, B. I. Jakobson, Glass composites reinforced with silicon-doped carbon
328 nanotubes. *Carbon* 128, 231 (2018).

329 ²⁵ Z. Wang, Q. Lv, S. Chen, C. Li, S. Sun and S. Hu, effect of interfacial bonding on
330 interphase properties in SiO₂/Epoxy nanocomposite: A molecular dynamics simulation study.
331 *Acs Appl. Mater. Interfaces* 8, 7499 (2016).

332 ²⁶ M. Kai, L. Zhang, K. Liew, Carbon nanotube-geopolymer nanocomposites: a molecular
333 dynamics study of the influence of interfacial chemical bonding upon the structural and
334 mechanical properties, *Carbon* 161 (2020) 772–783.

335 ²⁷. Davidovits, J., *Geopolymer Chemistry and Applications*. 2008: Geopolymer Institute.

336 ²⁸. Davidovits, J. Properties of geopolymer cements. In *First International Conference on*
337 *Alkaline Cements and Concretes*. 1994.

338 ²⁹ Z. Zuhua, Y. Xiao, Z. Huajun, C. Yue, Role of water in the synthesis of calcined kaolin-

339 based geopolymer, *Appl. Clay Sci.* 43 (2) (2009) 218–223.

340 ³⁰ M. Abdullah, K. Hussin, M. Bnhussain, K. Ismail, W. Ibrahim, Mechanism and chemical
341 reaction of fly ash geopolymer cement—a review, *Int. J. Pure Appl. Sci. Technol.* 6 (1) (2011)
342 35–44.

343 ³¹ P.S. Singh, M. Trigg, I. Burgar, T. Bastow, Geopolymer formation processes at room
344 temperature studied by ²⁹Si and ²⁷Al MAS-NMR, *Mater. Sci. Eng., A* 396 (1–2) (2005)
345 392–402.

346 ³² Y. Zhang, J.L. Zhang, J.Y. Jiang, D.S. Hou, J.R. Zhang, The effect of water molecules on
347 the structure, dynamics, and mechanical properties of sodium aluminosilicate hydrate
348 (NASH) gel: a molecular dynamics study, *Construct. Build. Mater.* 193 (2018) 491–500.

349 ³³ A.C. Van Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu, W.A. Goddard, ReaxFFSiO
350 reactive force field for silicon and silicon oxide systems, *J. Phys. Chem. A* 107 (2003) 3803–
351 3811.

352 ³⁴ M.A. Qomi, K. Krakowiak, M. Bauchy, K. Stewart, R. Shahsavari, D. Jagannathan, D.B.
353 Brommer, A. Baronnet, M.J. Buehler, S. Yip, Combinatorial molecular optimization of
354 cement hydrates, *Nat. Commun.* 5 (2014) 4960.

355 ³⁵ Y. Yu, B. Wang, M. Wang, G. Sant, M. Bauchy, Reactive molecular dynamics simulations
356 of sodium silicate glasses—toward an improved understanding of the structure, *Int. J. Appl.*
357 *Glas. Sci.* 8 (3) (2017) 276–284.

358 ³⁶ R. Dongol, L. Wang, A. Cormack, S. Sundaram, Molecular dynamics simulation of sodium
359 aluminosilicate glass structures and glass surface-water reactions using the reactive force field
360 (ReaxFF), *Appl. Surf. Sci.* 439 (2018) 1103–1110.

361 ³⁷ D.-C. Yue, T.-B. Ma, Y.-Z. Hu, J. Yeon, A.C. van Duin, H. Wang, J. Luo, Tribochemistry
362 of phosphoric acid sheared between quartz surfaces: a reactive molecular dynamics study, *J.*
363 *Phys. Chem. C* 117 (48) (2013) 25604–25614.

364 ³⁸ D.-C. Yue, T.-B. Ma, Y.-Z. Hu, J. Yeon, A.C. van Duin, H. Wang, J. Luo, Tribochemical
365 mechanism of amorphous silica asperities in aqueous environment: a reactive molecular
366 dynamics study, *Langmuir* 31 (4) (2015) 1429–1436.

367 ³⁹ K.L. Joshi, G. Psfogiannakis, A.C. Van Duin, S. Raman, Reactive molecular simulations
368 of protonation of water clusters and depletion of acidity in H-ZSM-5 zeolite, *Phys. Chem.*
369 *Chem. Phys.* 16 (34) (2014) 18433–18441.

370 ⁴⁰ G.M. Psfogiannakis, J.F. McCleerey, E. Jaramillo, A.C. Van Duin, ReaxFF reactive
371 molecular dynamics simulation of the hydration of Cu-SSZ-13 zeolite and the formation of
372 Cu dimers, *J. Phys. Chem. C* 119 (12) (2015) 6678–6686.

373 ⁴¹ M.C. Pitman, A.C. Van Duin, Dynamics of confined reactive water in smectite clay–zeolite
374 composites, *J. Am. Chem. Soc.* 134 (6) (2012) 3042–3053.

375 ⁴² J.L. Suter, L. Kabalan, M. Khader, P.V. Coveney, Ab initio molecular dynamics study of
376 the interlayer and micropore structure of aqueous montmorillonite clays, *Geochim.*
377 *Cosmochim. Acta* 169 (2015) 17–29.

378 ⁴³ M. Meo, M. Rossi, Prediction of Young's modulus of single wall carbon nanotubes by
379 molecular-mechanics based finite element modelling, *Compos. Sci. Technol.* 66 (11) (2006)
380 1597e1605.

381 ⁴⁴ A. Bagheri, A. Nazari, J.G. Sanjayan, P. Rajeev, W. Duan, Fly ash-based
382 boroaluminosilicate geopolymers: experimental and molecular simulations, *Ceram. Int.* 43 (5)
383 (2017) 4119–4126.

384 ⁴⁵ A-T. Akono, Fracture behavior of metakaolin-based geopolymer reinforced with carbon
385 nanofibers, *Ceram. Int J Ceramic Eng Sci.* 2020;2:234–242.

386 ⁴⁶ P. Jittabut, S. Horpibulsuk, Physical and microstructure properties of geopolymer
387 nanocomposite reinforced with carbon nanotubes, *Mater. Today: Proc.* 17 (2019) 1682–1692.

388 ⁴⁷ M. Hassanzadeh-Aghdam, M. Mahmoodi, R. Ansari, Creep performance of CNT polymer
389 nanocomposites -An emphasis on viscoelastic interphase and CNT agglomeration,
390 *Composites Part B* 168, 2019, 274–281.

391 ⁴⁸ M. Hasanzadeh, R. Ansari, M.K. Hassanzadeh-Aghdam, Evaluation of effective properties
392 of piezoelectric hybrid composites containing carbon nanotubes, *Mechanics of Materials* 129,
393 2019 63–79.

394 ⁴⁹ J. Lu, M. Luo, B.I. Yakobson, Glass composites reinforced with silicon-doped carbon
395 nanotubes, *Carbon* 128 (2018) 231–236.

396 ⁵⁰ N.V. Medhekar, A. Ramasubramaniam, R.S. Ruoff, V.B. Shenoy, Hydrogen bond networks
397 in graphene oxide composite paper: structure and mechanical properties, *ACS Nano* 4 (4)
398 (2010) 2300–2306.

399 ⁵¹ Q. Pei, Y. Zhang, V. Shenoy, A molecular dynamics study of the mechanical properties of
400 hydrogen functionalized graphene, *Carbon* 48 (3) (2010) 898–904.

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408 **Tables**

409 **Table 1:** Chemical composition of metakaolin geopolymer.

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<i>Si/Al ratio</i>	<i>SiO₂ (wt%)</i>	<i>Al₂O₃ (wt%)</i>	<i>Na₂O (wt%)</i>	<i>H₂O (wt%)</i>	<i>Density (g/cm³)</i>
3	48.60	27.40	16.30	7.70	2.00

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414 **Table 2:** Diffusion coefficients of pristine CNT, CNT-oxide and Na⁺ cations in
415 CNT/geopolymer matrix.

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Component	Diffusion coefficient 10⁻¹¹ (m²/s)	Other calculations 10⁻¹¹ (m²/s)
Pristine CNT	0.051	
CNT-oxide	0.166	
Na⁺	0.376 (pristine CNT) 1.113 (CNT-oxide)	0.345 ²⁶

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Figure captions

Figure 1: CNT/geopolymer model. The cyan, blue, green, red, yellow, white and orange spheres represent Si, Al, Na, O, H and C atoms, respectively.

Figure 2: (a) Atomic structure of Pristine (6,6) carbon nanotube, and (b) 10% doped CNT-oxide.

Figure 3: Variation of elastic modulus of CNT/geopolymer nanostructure with pristine CNT concentration.

Figure 4: Indentation modulus of CNT/geopolymer versus pristine CNT dosage.

Figure 5: Bulk density of the nanostructure as a function with CNT concentration.

Figure 6: Interfacial energy variation with CNT content.

Figure 7: Young modulus of CNT and CNT-oxide with various doping concentrations.

Figure 8: Unit cell of 10% doped CNT-oxide/geopolymer: (a) side view structure; (b) cross section structure showing the multiple links between CNT and geopolymer matrix; (c) zoom in perspective view of the nanostructure, where the C atoms connect with O atoms in the geopolymer structure (yellow Si, blue Al, green Na, red O, white H, grey-blue C).

Figure 9: Elastic modulus of functionalized CNT/geopolymer as function of doping CNT-oxide concentrations.

Figure 10: Effect of doping CNT-oxide dosage variation on the bulk density of functionalized CNT/geopolymer.

Figure 11: Mean Square Displacement of (a) pristine and functionalized CNT component and (b) Na⁺ cation versus time simulation.

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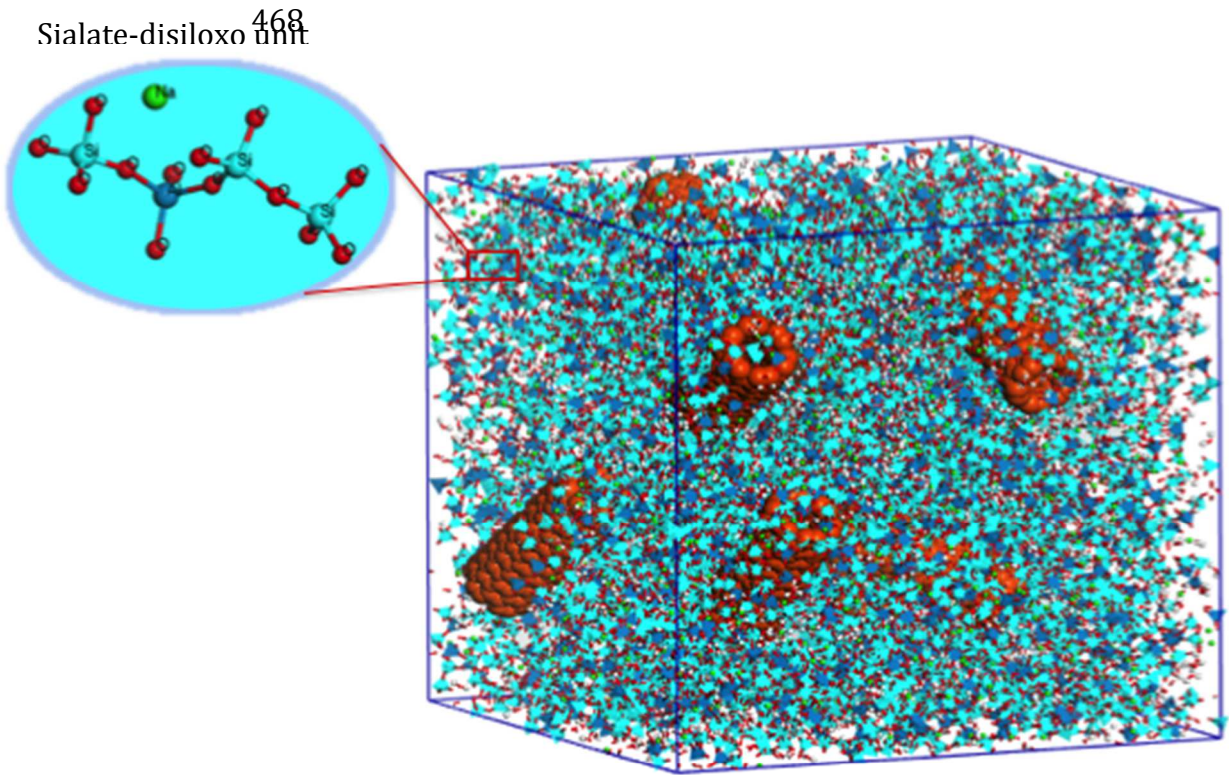
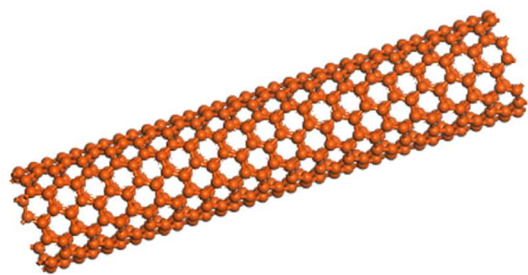
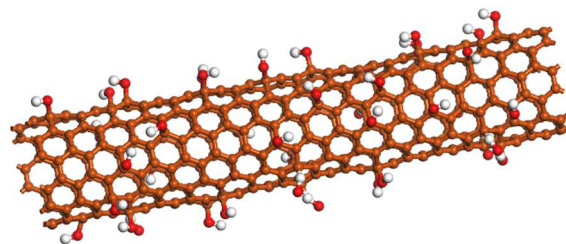


Figure 1

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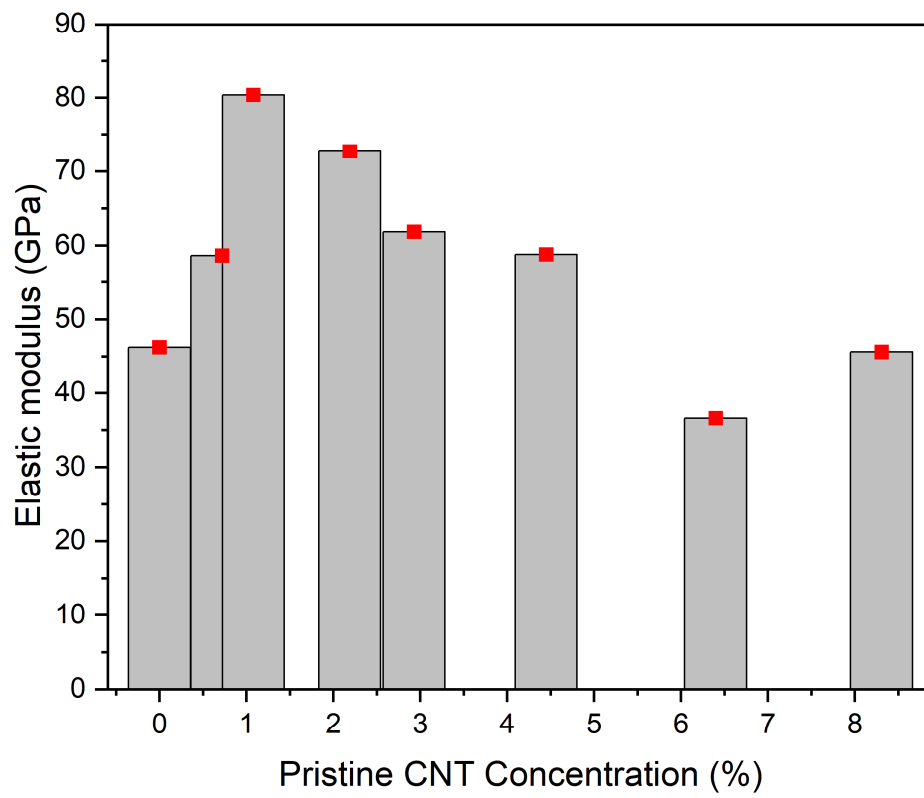


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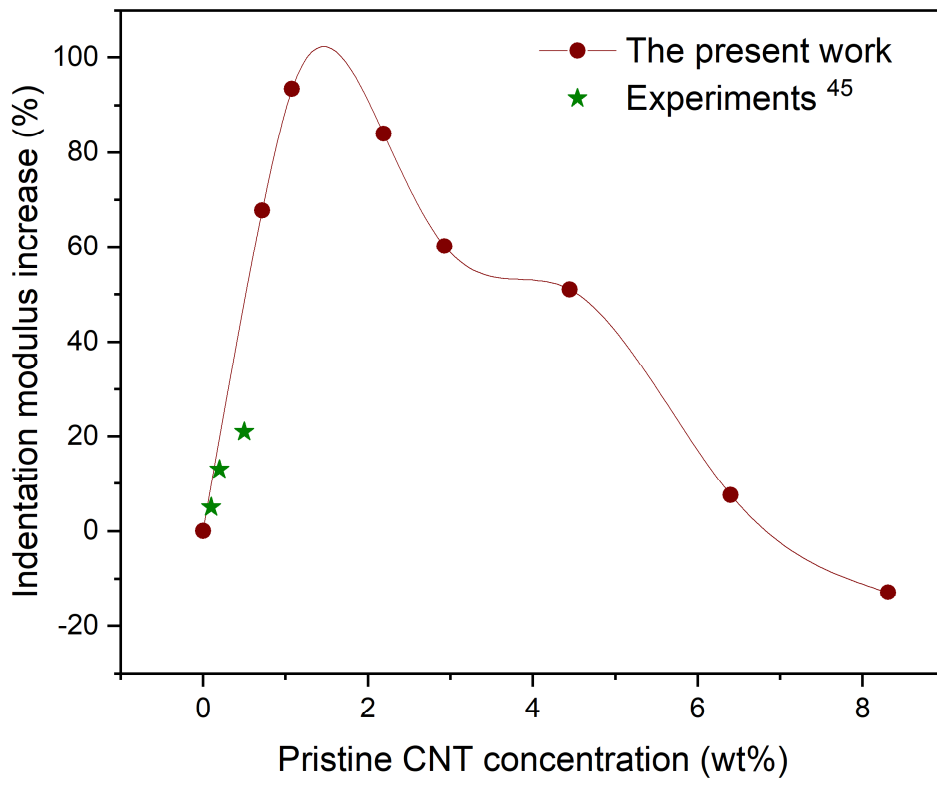
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Figure 2



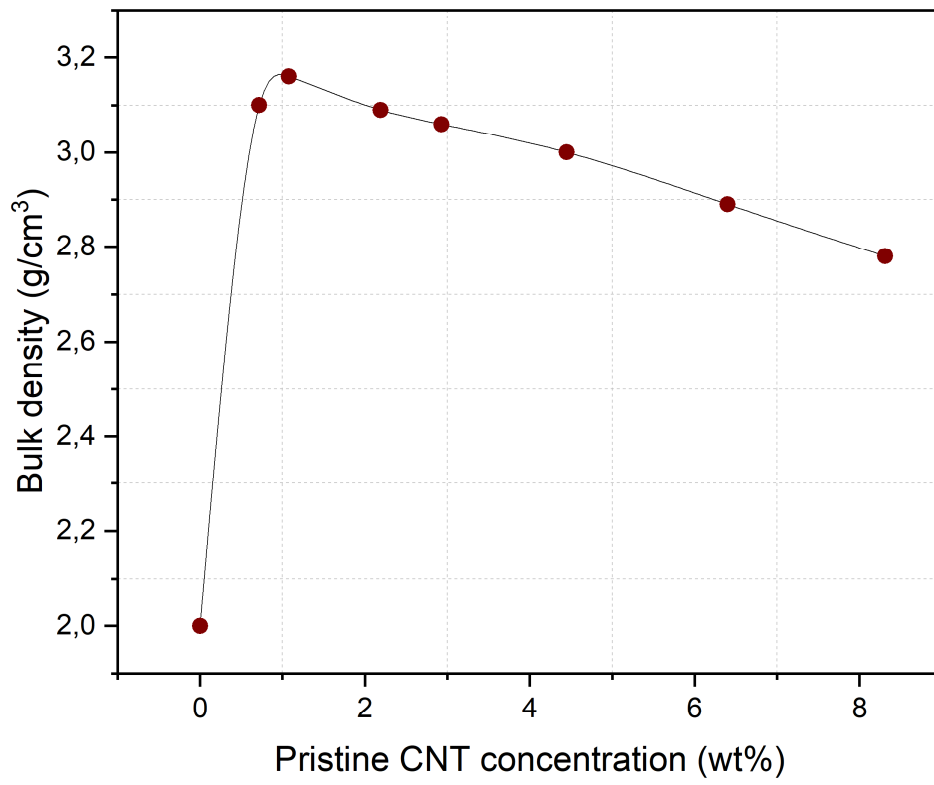
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Figure 3



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Figure 4



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Figure 5

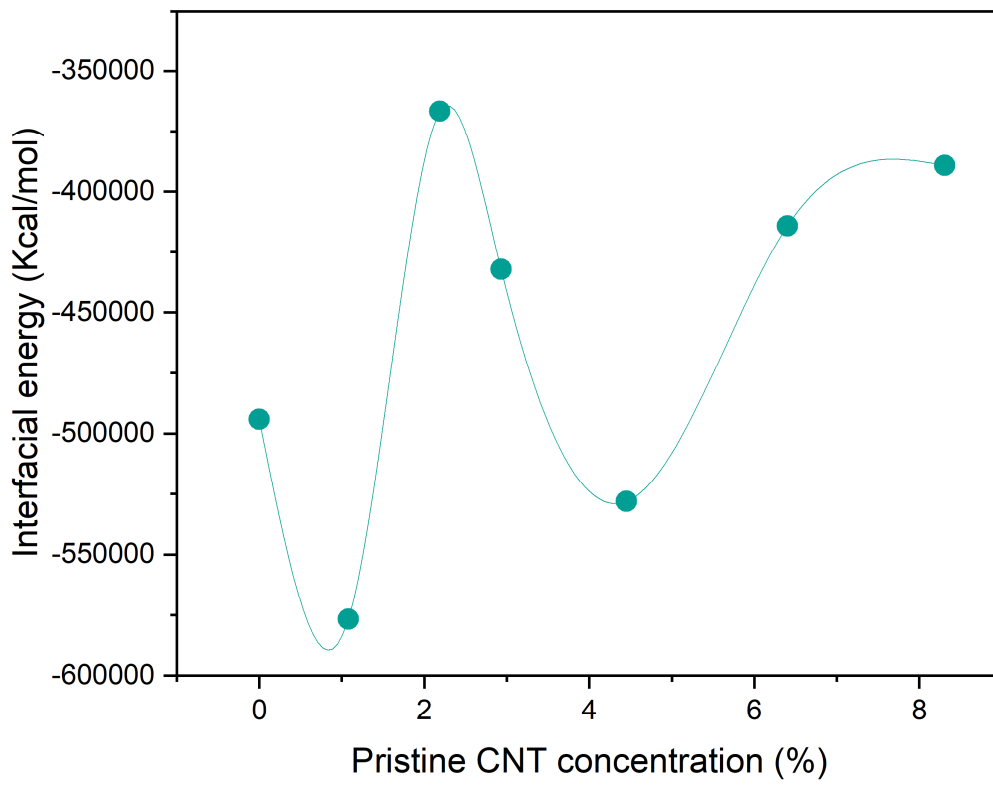
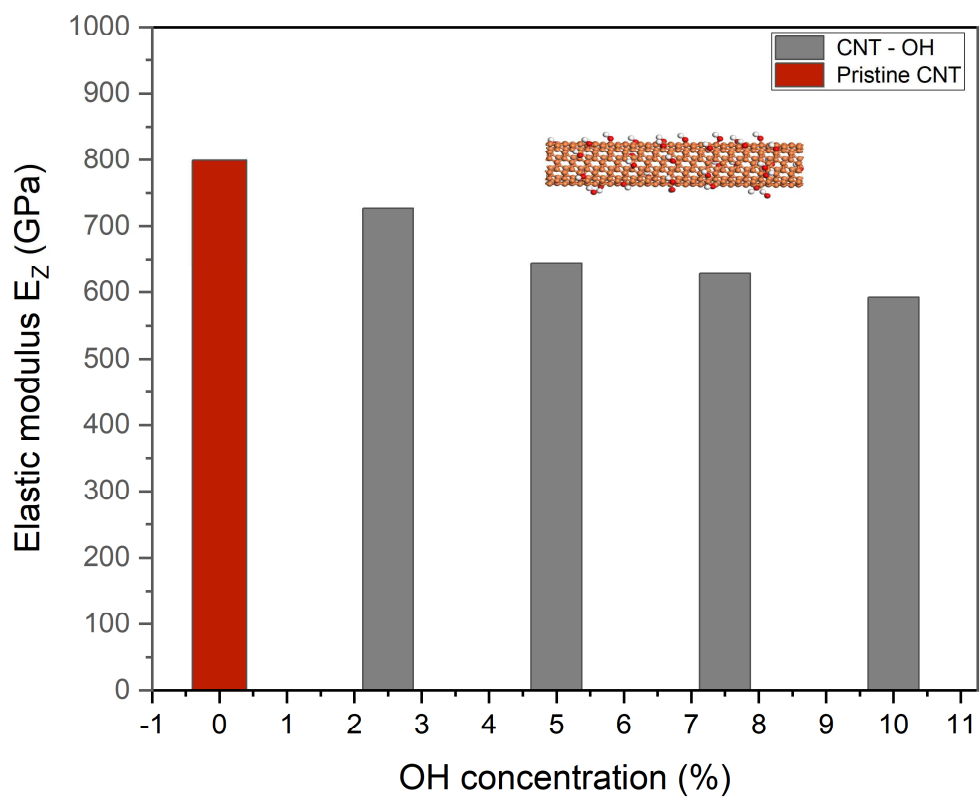


Figure 6

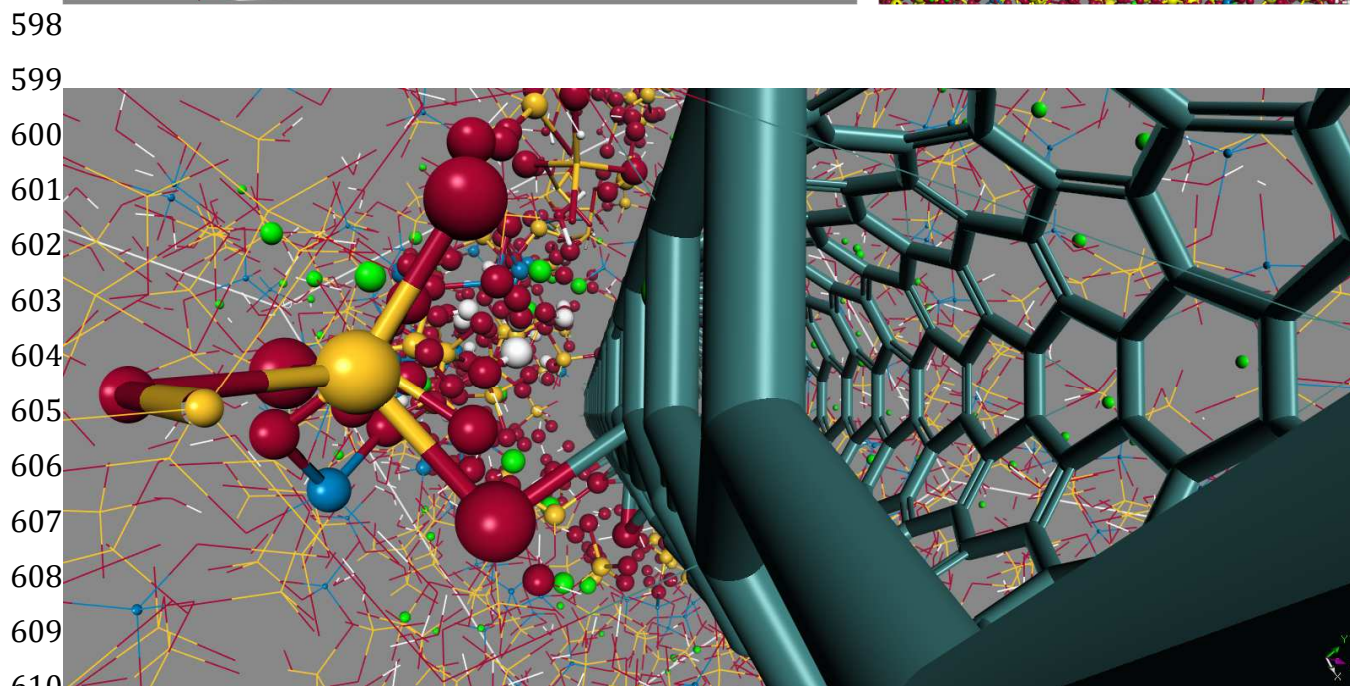
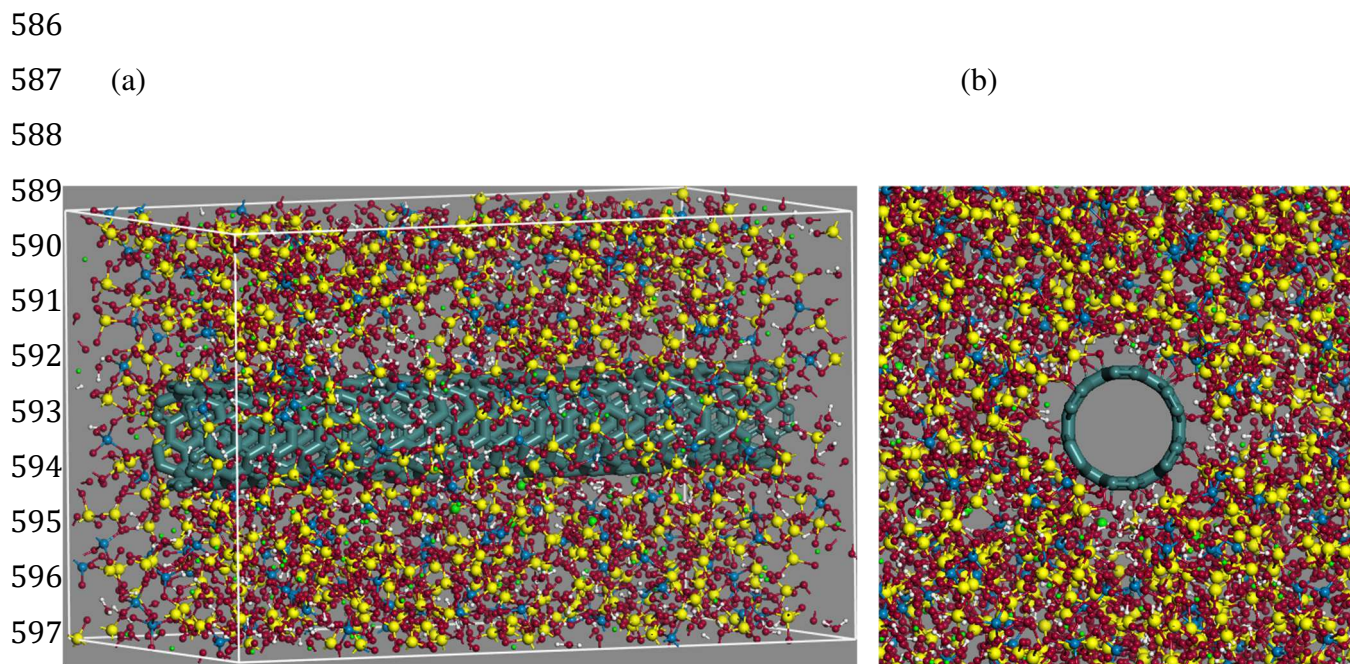
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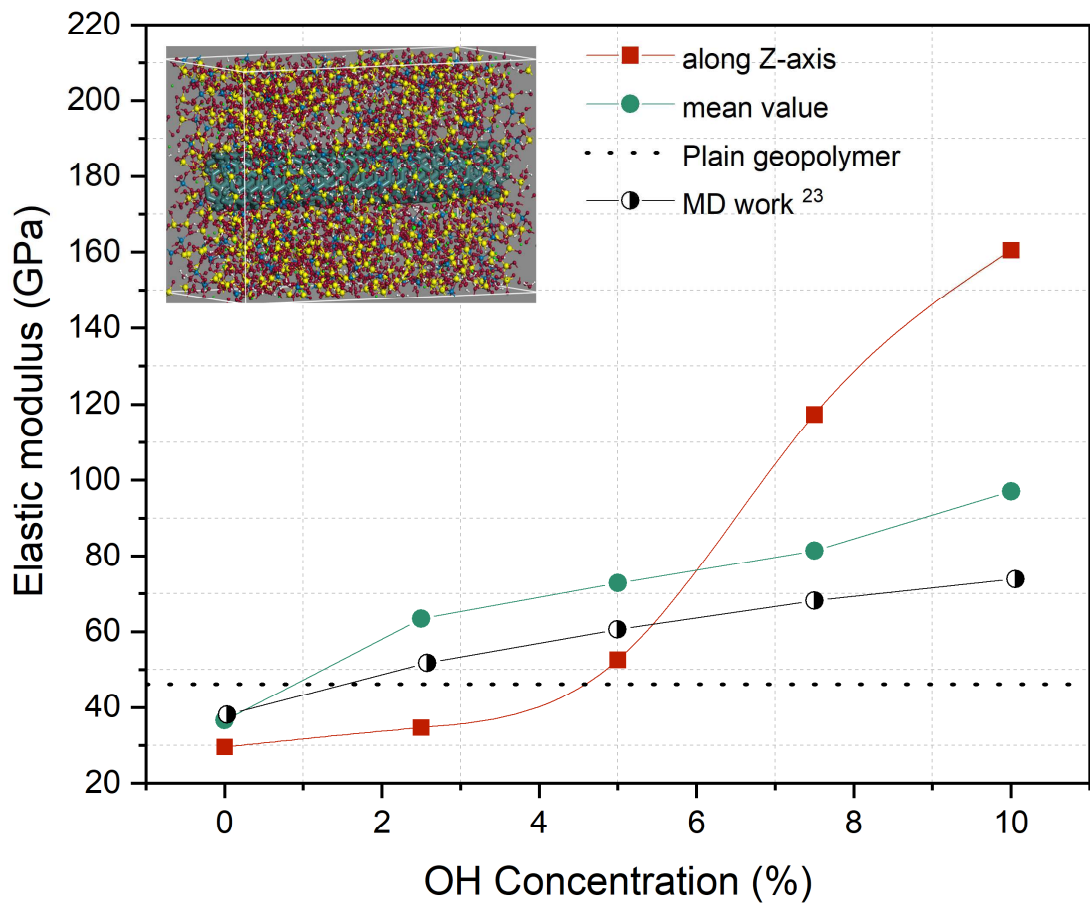
Figure 7



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Figure 9

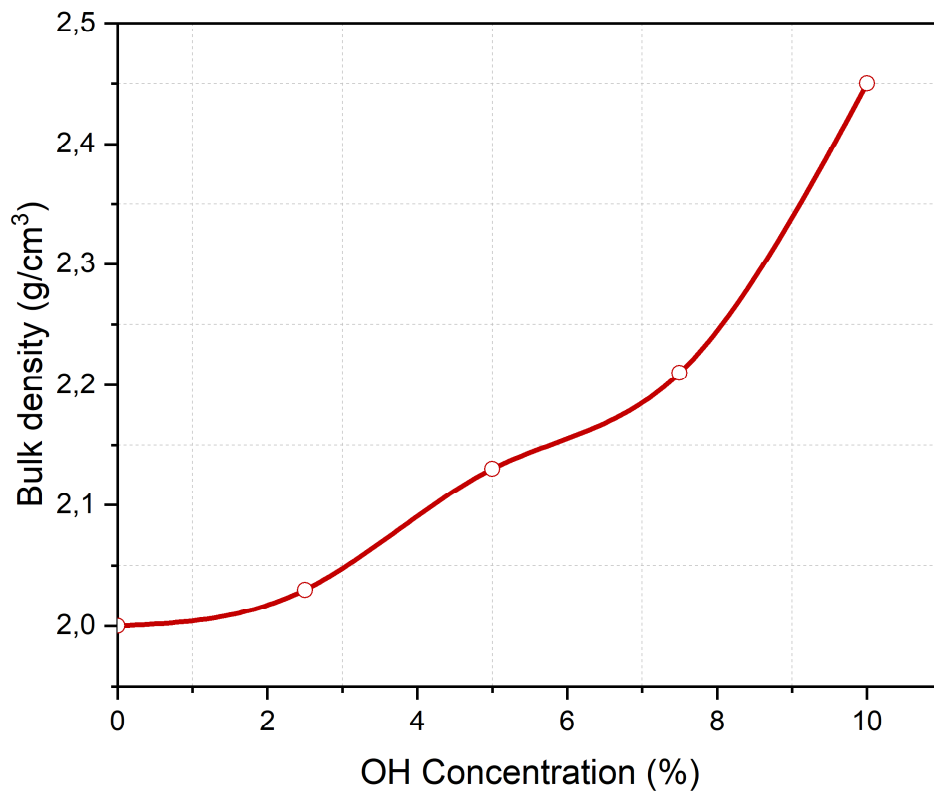
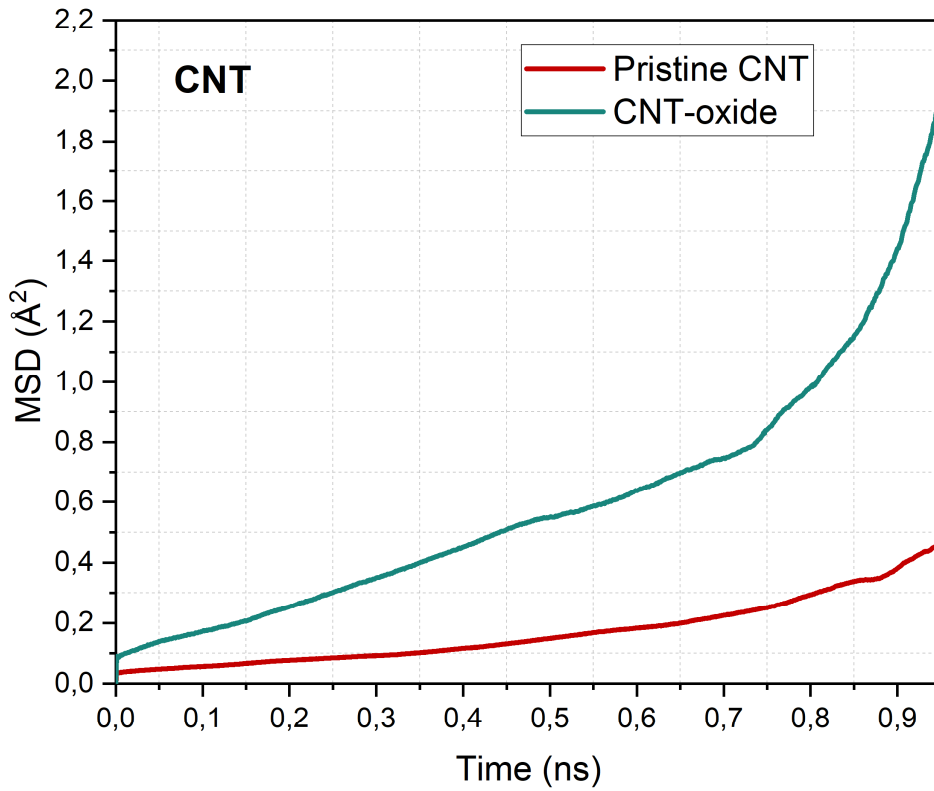


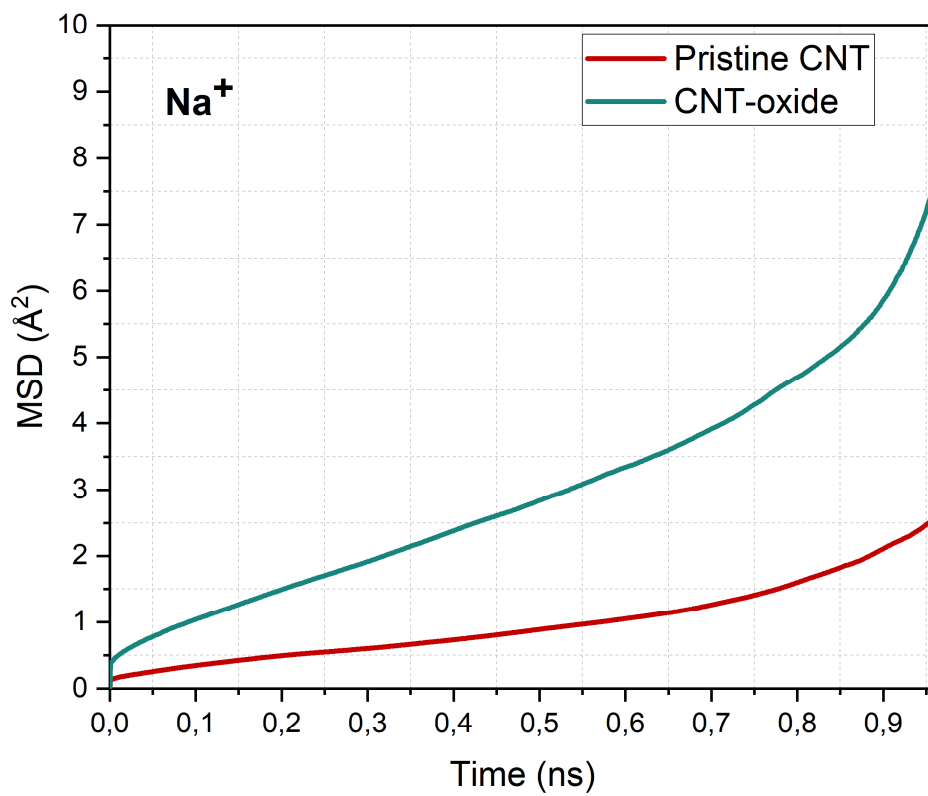
Figure 10

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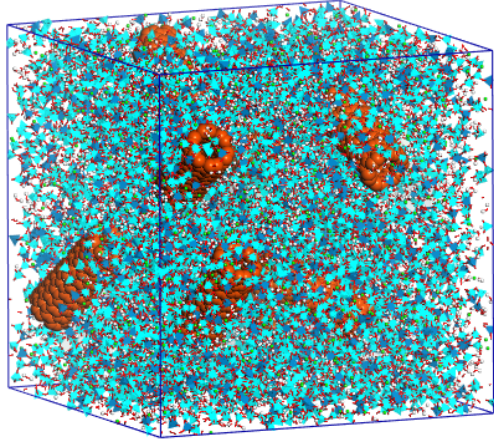
(a)



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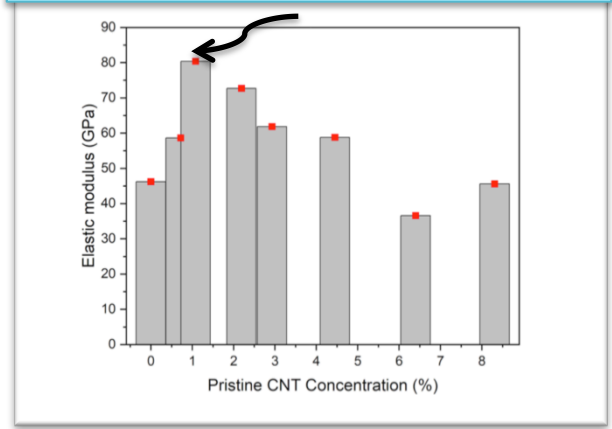
Figure 11

CNT/geopolymer nanostructure

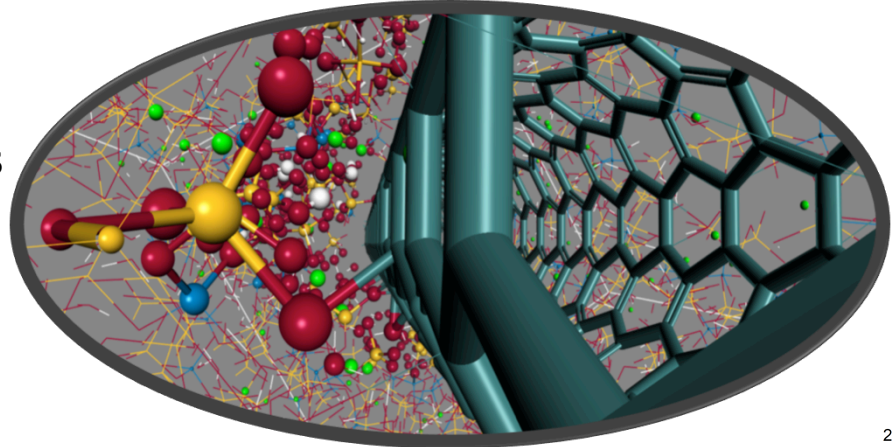


Enhancement up to 74%

Optimum CNT concentration

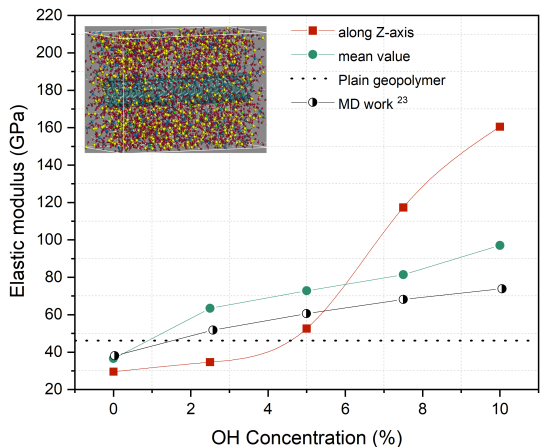


Functional CNT/geopolymer



Mechanical properties

A raise of 165%



Dynamical properties

Faster CNT diffusion

