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Polymer interfaces with carbon nanostructures: First principles density functional theory and molecular dynamics study of polyetheretherketone adsorption on graphene and nanotubes

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ABSTRACT

The interface of polyetheretherketone (PEEK) with carbon nanotubes (CNTs) and graphene is investigated using density functional theory and molecular dynamics within the REAXFF-Ig interatomic interaction framework. The dependence of PEEK adsorption energy on the polymer chain length, temperature, starting adsorption configuration of the fully stretched conformation, and on the nature of the substrate was investigated. Overall, the interface between graphene and the polymers yield larger adsorption energies than the CNTs. Adsorption energies decrease with increasing temperature while for the CNT substrates, there is a slight dependence on the initial relative orientation between the nanotubes and the extended polymer chain. This is the first study on this interface, to the best of the authors' knowledge, with such a wide spectrum of relevant variables.

1. Introduction

The extraordinary materials properties of nanotubes such as high axial Young's modulus [1], porosity [2] and electronic structure [3] can be suitably coupled with those of polymers to enhance polymer performance [4–8]. One of the most common applications is the reinforcement of the mechanical properties of polymer matrices with the introduction of carbon nanotubes (CNTs) [9,10]. At the same time, polymers may also be used to modify the properties of CNTs. For instance, wrapping a long polymer chain around a CNT has been observed to increase the buckling strength of the nanotube [11]. Other important applications are the improvement of dispersion [12] and selectivity [13] of the CNTs, which tend to form bundles in solution. Recently, solar cells have been designed that use the controllable charge transfer at the interface between the CNTs and P3HT [14]. As a final recent example of the vast possibility of applications, we mention a targeted drug delivery method developed for cancer drugs using the CNT interface with the effective component of the drug [15].

Among the endless list of technologically important polymers, we chose polyetheretherketone (PEEK) as a test case, due to the fact that it has been investigated theoretically in relatively few studies in spite of its

many desirable properties [16,17]. PEEK is a high-performance thermoplastic polymer with a broad range of applications, such as in dentistry [18,19], tribology [20], and in implants [21]. Its mechanical properties, chemical resistance, and relatively high melting temperature make it a viable material for use in the aircraft and spacecraft industries [22,23].

Theoretical studies of graphene/polymer and CNT/polymer interfaces are performed at multiple scales ranging from coarse-grained methods such as representative volume elements [24] to the fully quantum mechanical treatment at the density functional theory (DFT) level [25]. Here we study the properties of the graphene/PEEK and CNT/PEEK interfaces with both DFT and molecular dynamics (MD), with the aim to study the dependence of the adhesion strength of PEEK chains on the carbon-based nanostructures on a range of parameters such as temperature, chain length, and the length, radius and type (armchair vs zigzag) of the CNT substrate. We present a bottom-up approach, starting with the smallest aromatic ring units constituting a single PEEK monomer. This allows us to understand the relative effect of each ring in the interaction with the substrate. We then build our results up to a single PEEK monomer and finally to 3-, 6- and 9-monomer chains. For the PEEK subunits and the single PEEK monomer, we

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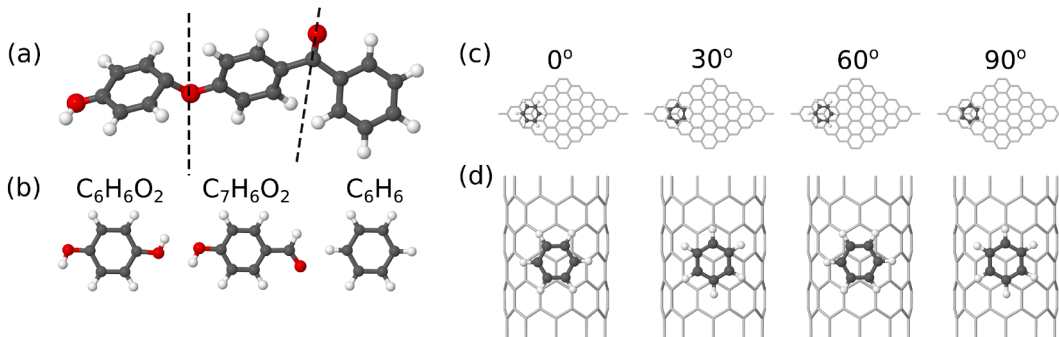


Fig. 1. a single PEEK monomer (a) divided into the three subunits $C_6H_6O_2$, $C_7H_6O_2$, and C_6H_6 (b). C_6H_6 adsorption geometries on graphene (c) and a (10,0) CNT for four distinct orientation angles (d). The zero-angle orientation convention for the other two molecules is reported in Fig. S1 of the SI.

investigate their adhesion properties on graphene and CNT substrates using DFT calculations. DFT not only provides an accurate description of the interface at hand but it is also used to benchmark our MD protocol that we use to study the adsorption of the longer polymer chains.

Our MD calculations employ the reactive force-field (ReaxFF) [26], which was originally developed to accurately describe challenging reactive processes. Due to its high transferability thanks to bond-order dependence and dynamically updated atomic charges, its domain of applications has rapidly expanded to include a very diverse collection of systems [27], including nonreactive cases [28]. In fact, it was recently employed in the modelling of crystalline and amorphous PEEK [17]. We employ the REAXFF-Ig (low gradient) variant [29] with improved long-range behavior for a better description of van der Waals interactions.

The paper is organized as follows: the computational methods are described in the next Section 2, which contains a detailed description of the MD protocol. We then present a discussion of our results in Section 3, while conclusions and perspectives are given in the final Section 4.

2. Computational methods

The energetics of adsorption and the adsorption geometries of a single PEEK monomer and its three aromatic subunits (C_6H_6 , $C_7H_6O_2$, and $C_6H_4O_2$, see Fig. 1) on graphene and several CNTs were investigated within DFT. All DFT calculations were performed using the open source code suite Quantum ESPRESSO [30]. Ultrasoft pseudopotentials were used to treat the interaction between the nuclei and the electrons [31] and van der Waals interactions were included via the nonlocal exchange correlation functional vdW-DF1 [32] with the C09 correction developed by Cooper [33]. A kinetic energy cutoff of 30 Ryd was employed for all calculations and a vacuum distance of at least 11 Å was introduced to avoid interaction between periodic images. Subunit and monomer adsorption on graphene were studied using 6×6 and 8×8 simulation cells, respectively. For these calculations a $3 \times 3 \times 1$ Monkhorst-Pack [34] (MP) grid was used for Brillouin zone integrations. For the adsorption on CNT substrates, $1 \times 1 \times 8$ MP grids were used for all CNT/subunit interfaces while $1 \times 1 \times 4$ MP grids were used for the calculations involving the PEEK monomer. Adsorption energies, E_b , were calculated using

$$E_b = E_t - E_s - E_a \quad (1)$$

where E_t , E_s and E_a are the energies of the total system, the substrate (graphene or CNT) and the isolated adsorbate, respectively. The total energy of the isolated adsorbate was calculated using a large cubic unit cell at the Γ point of the Brillouin zone.

The interaction of the PEEK aromatic subunits, the monomer and the polymer chains with both graphene and CNTs were modeled using MD as implemented in the LAMMPS Molecular Dynamics Simulator [35,36]. Bonded and nonbonded interactions were all modeled within the unified framework of the ReaxFF-Ig force field [26,29]. An initial static

minimization using the conjugate gradient algorithm was followed by the evolution of the system in an NVT ensemble. Quantities of interest, such as the adsorption energy, were calculated as an average over a suitable number of snapshots of the final portion of this NVT ensemble evolution stage. Equations of motion were integrated using the velocity Verlet algorithm [37] and temperature control was achieved by the Berendsen thermostat [38] with a damping time of 0.1 ps. A time step of 0.1 fs was used in all our MD calculations. The coupling of the Berendsen thermostat and ReaxFF is a popular protocol in literature [39].

The length of the NVT evolution stage as well as the elapsed time between the snapshots considered in the averaging process varied with system size. Subunits of PEEK and the full PEEK monomer were allowed to interact with CNTs and graphene for 200 ps. The average adsorption energy was calculated from ten equally spaced snapshots taken from the last 50 ps of the simulation. In the MD simulations on the 3-, 6- and 9-unit PEEK oligomers in isolation (i.e. without any substrate) the systems were kept at 10 K using the Berendsen thermostat (damping parameter of 100 fs) for 1 ns with a time step of 0.1 fs. We monitored the end-to-end distance and radius of gyration during the entire length of the simulation. The initial configurations of the polymers were constructed using the online nanoHUB Polymer Modelling Tool [40], which utilizes configurational bias Monte Carlo (MC) [41].

For calculations involving 3-, 6-, and 9-unit PEEK chains adsorbed on graphene and CNT substrates, the total simulation time was increased from 200 ps to 400 ps and the adsorption energies were calculated using 10 snapshots taken at equal intervals in the last 100 ps. The positions of the atoms constituting the graphene and CNT substrates were held fixed during all calculations. With increasing chain length of the polymer, the CNT length was also increased to 5 nm, 10 nm and 15 nm, respectively, to reduce the interaction between periodic images as much as possible. Adsorption energies were once again calculated using the expression in Eq. (1) where E_t , E_s and E_a are interpreted as the average potential energy of the full system, the static potential energy of the graphene or CNT substrate and the static potential energy of the molecule in the configuration taken from each particular snapshot, respectively.

All calculations were conducted on periodic graphene and CNT substrates of sufficient length so as to minimize the lateral interactions between neighboring simulation cells. In addition to adsorption energies, we also report the end-to-end distance and the radius of gyration of the 3-, 6- and 9-unit PEEK chains both in isolation and in contact with the substrates. The end-to-end distance is simply the distance between the two ends of the polymer while the radius of gyration is defined by

$$R_g^2 = \frac{1}{M_T} \sum_{n=1}^N m_n (\mathbf{R}_n - \mathbf{R}_{COM})^2, \quad (2)$$

where M_T is the total mass of the polymer, m_n is the mass and $\mathbf{R}_n$ is the position vector of the n th atom, while $\mathbf{R}_{COM}$ is the position of the center of mass of the polymer. Both the end-to-end distance and R_g^2 can be used as measures for the degree of folding of the polymer onto itself.

Table 1

DFT adsorption energies, E_b (meV/molecule), and adsorption distances (d , Å) of $C_7H_6O_2$, $C_6H_6O_2$ and C_6H_6 on graphene and on a (10,0) CNT. Values in boldface indicate the most stable orientations for each molecular fragment.

	Graphene			(10,0) CNT		
	$C_7H_6O_2$	$C_6H_6O_2$	C_6H_6	$C_7H_6O_2$	$C_6H_6O_2$	C_6H_6
0°	-848.1	3.27	-778.3	3.23	-616.8	3.28
30°	-830.0	3.28	-769.5	3.25	-613.0	3.29
60°	-837.3	3.27	-778.1	3.24	-616.9	3.28
90°	-862.7	3.24	-768.7	3.24	-613.0	3.29

Table 2

DFT adsorption energies for a single PEEK monomer adsorbed on CNTs and on graphene. For each CNT, its axial length (l , Å) and its radius (R , Å) are reported. Energies in eV.

(n,m)	l	R	E_b
(10,0)	13.05	3.99	-1.317
(10,0)	21.75	3.99	-1.255
(10,0)	26.01	3.99	-1.264
(12,0)	26.01	4.79	-1.297
(15,0)	26.01	5.99	-1.325
(6,6)	25.11	4.15	-1.293
(7,7)	25.11	4.84	-1.303
(8,8)	25.11	5.53	-1.333
Graphene	—	—	-1.409

3. Results and discussion

3.1. DFT calculations for monomer adsorption

To obtain a deeper understanding of the interfaces, we start with a detailed account of the interaction between a single PEEK monomer and the carbon-based substrates. First, we divide the monomer into the three constituent subunits, as displayed in Fig. 1(a) and (b). Extra H atoms were added to the O terminations to obtain 4-hydroxybenzaldehyde ($C_7H_6O_2$), and 1,4-dihydroxybenzene ($C_6H_6O_2$). We explore different orientations of all three subunits on both a flat sheet of graphene and a (10,0) CNT. In doing so, we define the zero of the orientation angle as seen in Fig. 1(c-d) and Fig. S1 of the SI. The adsorption energies for all orientations are reported in Table 1.

The adsorption energies of the PEEK subunits on graphene are more

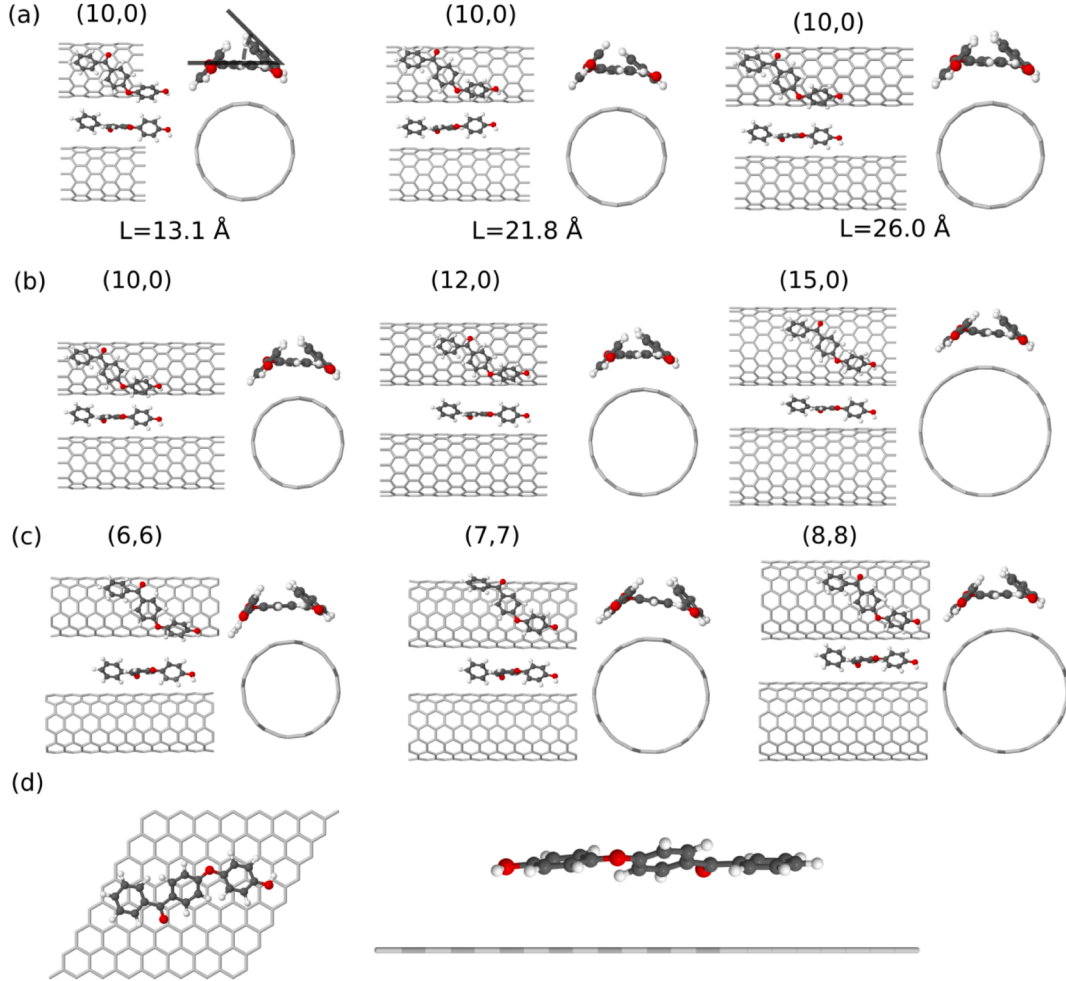


Fig. 2. Optimized geometries (side, top and front views) of the CNT/PEEK interfaces obtained through DFT (a–c). (a) (10,0) CNT of three lengths, (b) zigzag CNTs ($l = 26.0$ Å), and (c) armchair CNTs ($l = 25.1$ Å). The angle of inclination of the terminal aromatic rings is illustrated in the upper left panel. (d) The PEEK monomer on an 8×8 graphene substrate from the top and from the side.

than 100 meV larger than on the CNTs. This result is a direct consequence of the increased area of contact of the molecule with the substrate for graphene compared to CNT, which is reduced in the latter, due to its curvature. The distances reported in Table 1 are the average distance of the six atoms constituting the aromatic ring on each molecule to the graphene (CNT) C atom directly below the center of the ring. In the case of benzene, the 0° and 60° results as well as the 30° and 90° results are very similar due to symmetry.

Following this preliminary work, the adsorption energies of the PEEK monomer were calculated on graphene and several CNT substrates as reported in Table 2. Due to the periodic geometry of our simulation cells, their length were adjusted such as to minimize interaction between periodic images. The effect of CNT length on the adsorption energies was also investigated by calculating PEEK adsorption energies on a (10,0) zigzag CNTs with three different lengths. In addition, the energetics of adsorption of the monomer were calculated for CNTs of different radii and chiralities. The adsorption geometries are presented in Fig. 2.

The initial configurations of the PEEK monomer on the substrates were taken from 1 ns-long MD simulations at 10 K. Each system was then subjected to a further geometry optimization using DFT. In the calculation of the adsorption energies using Eq. (1), the energy of the isolated adsorbate, E_a , was calculated, at its adsorption geometry, in a large cubic simulation box and performing a single-step self-consistent field run. This way of calculating E_b eliminates the contribution to the adsorption energy associated with the distortion of the molecule during the process, and includes only its interaction energy with the substrate. For the (10,0) CNTs (upper panels of Fig. 2), we observe a decrease of approximately 0.06 eV in E_b in going from the smallest length to the next. This is due to the reduction in the lateral interaction between periodic images. For the two larger sizes, however, the lateral interactions appear to be eliminated and there are no significant changes in E_b .

The effect of CNT radius on computed E_b is investigated next, by comparing the adsorption energies on (10,0), (12,0), and (15,0) zigzag CNTs having the same axial length of 26.01 Å (panels (b) of Fig. 2). Adsorption energies increase very slightly with increasing CNT diameter (i.e. with decreasing curvature). As shown in Fig. 2, upon adsorption the terminal aromatic rings of the monomer form an angle of around 50° with respect to the central ring, and in opposite directions. This configuration maximizes the contact area for all three subunits with the CNTs surface while at the same time minimizing the H-H repulsion. However, the computed E_b for PEEK adsorption is smaller than the sum of the adsorption energies of its components.

As a means of understanding the effect of CNT type (zigzag vs armchair) on the energetics of PEEK monomer adsorption, three armchair nanotubes with (m, m) indices of (6,6), (7,7), and (8,8) were also selected, with radii nearly equal to those of the previously studied (10,0), (12,0) and (15,0) CNTs, respectively. Their axial lengths were also kept as close as possible at 25.1 Å. Similarly to the zigzag CNTs, the adsorption energy was found to increase very slightly as a function of CNT radius also in the case of the armchair nanotubes. The armchair and zigzag nanotubes yield very similar energies within a few meV.

The adsorption geometry of the PEEK monomer on a flat graphene substrate is shown in the lower panels of Fig. 2 while E_b values are reported in Table 2. In this case, the angles that the three PEEK subunits form with the flat graphene surface are about 10°, 20° and 7° in opposite directions, and are significantly smaller than the values observed for PEEK adsorption on CNTs. Furthermore, the E_b of 1.41 eV computed for this configuration is larger by at least 80 meV than that for CNTs.

3.2. MD calculations for polymer adsorption

Before starting the MD production runs, our protocol was benchmarked against the DFT E_b values obtained for the monomer subunits and a single PEEK unit. The adsorption energies of benzene, $C_7H_6O_2$ and $C_6H_6O_2$ on a (10,0) CNT of length 13.05 Å were calculated at 0 K, 100 K

Table 3

DFT and MD interaction energies (in eV) for the PEEK monomer adsorbed on graphene and on CNTs with different radii. For MD, E_b values are reported at three different temperatures

	DFT	ReaxFF		
		0 K	100 K	300 K
(10,0)	-1.27	-1.35	-1.39	-1.39
(12,0)	-1.30	-1.45	-1.47	-1.09
(15,0)	-1.33	-1.55	-1.48	-1.42
(6,6)	-1.29	-1.40	-1.47	-1.22
(7,7)	-1.30	-1.48	-1.36	-1.40
(8,8)	-1.33	-1.52	-1.52	-1.21
Graphene	-1.41	-1.27	-0.88	-0.70

and 300 K, and the results, along with a comparison of the most favorable configurations identified using DFT, are presented in Table S1 of the SI.

ReaxFF calculations at $T = 0$ K are in good agreement with the DFT results, although the ReaxFF E_b values are, on average, higher in magnitude. A similar trend can be seen in the comparison between DFT and MD results for the adsorption of the PEEK monomer, summarized in Table 3. Focusing on the MD results, at lower temperatures (0 K and 100 K), the E_b values increase with increasing radius; at the higher temperature of 300 K, the polymer has instead sufficient thermal energy to explore more low-energy configurations and, as a result, the trend is not necessarily obeyed. In particular, dihedral angles between the aromatic subunits of the monomer assume values that greatly differ from those characteristic of the configurations found at lower temperatures. Selected adsorption geometries are reported in Fig. S2 of the SI.

MD simulations were run for isolated oligomers (containing 3, 6, and 9 PEEK units), with the goal of obtaining insight into the strength of the intramolecular interactions. The relative stability of the adsorption geometries of the polymers on CNTs and graphene is expected to be governed by an interplay between intramolecular forces and the interaction with the substrates. The initial and final configurations, taken from the very last step of the complete MD runs, along with the end-to-end distance and radii of gyration are presented in Fig. 3.

For the three oligomers, the equilibrium configurations were found to deviate heavily from their initial linear arrangements and fold onto themselves as evidenced also by the plots of end-to-end distances and radius of gyration. Folding occurred not gradually but mostly via abrupt changes in the geometry. As expected, the 3-monomer chain has the smallest radius of gyration. In contrast, the radius of gyration of the 9-monomer chain is similar to the 6-monomer chain, both between 10 and 15 Å.

Finally, the geometry and energetics of adsorption of the 3-, 6-, and 9-unit polymers on the flat graphene sheet and on a (8,8) nanotube were investigated using the same MD protocol. In addition to the length of the chains, dependence on two more parameters, namely temperature and the starting angle that the rod-like polymer forms with respect to the axis of the nanotube, were investigated. A schematic representation of this angle is reported in Fig. S3 of the SI. The starting angle that the rod-like polymer forms with respect to the bottom edge of the rectangular graphene simulation cell was instead chosen to be 45° for all calculations. This minimizes the initial end-to-end interaction of the fully stretched polymers in neighboring simulation cells. Once the simulation starts, the polymer folds immediately and intra-cell interaction ceases to be an issue. For these systems, snapshots were taken between 300–400 ps at every 10 ps of the simulation run. Simulations were conducted at three different temperatures (100 K, 300 K and 500 K) and, for the CNT samples, with three different initial angles (0°, 45° and 90°).

The configurations obtained at the end of each simulation are displayed in Fig. 4 for the 9-monomer chain and an initial starting angle of 0° for the CNT substrate. Similar figures for the other two oligomers are reported in Fig. S4 of the SI, while results for the 9-monomer chain on a (8,8) CNT at 500 K for three initial starting angles are displayed in

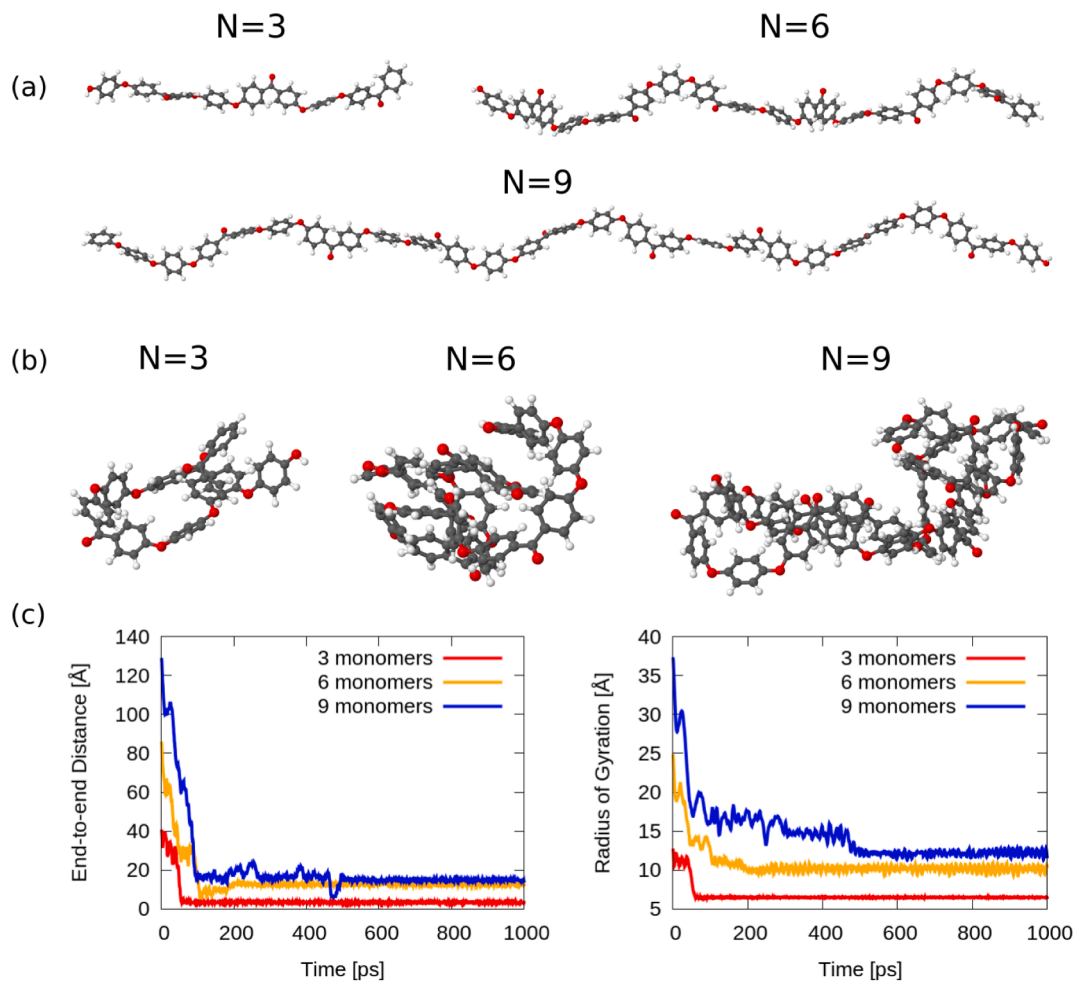


Fig. 3. The initial (a), and the final (b) configurations of the isolated oligomers containing 3, 6, and 9 PEEK units respectively. The end-to-end distance and radius of gyration data from the NVT run (c).

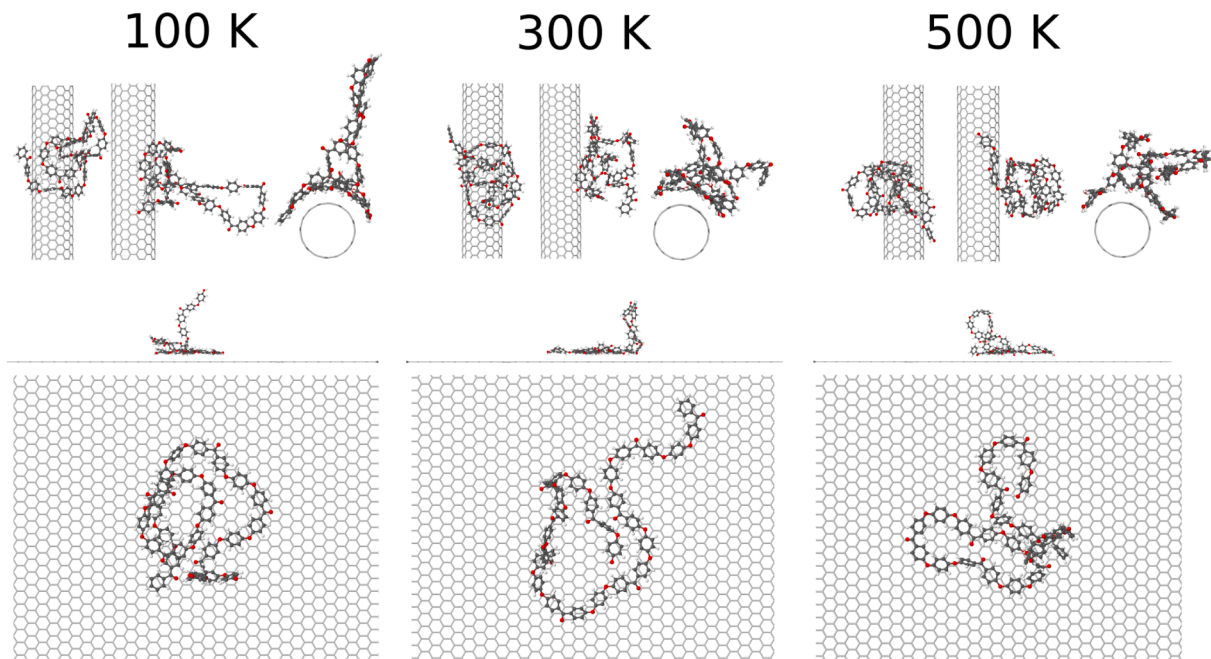


Fig. 4. The final configuration of the 9-monomer PEEK chain on the (8,8) CNT (top panels) and graphene (bottom panels) at temperatures of 100 K, 300 K, and 500 K. The starting angle (as defined in Fig. S3 of the SI for the CNT substrate) were taken to be zero for all simulations on the CNT substrate.

Table 4

Average adsorption energies (in eV) of rod-like PEEK chains adsorbed on a (8,8) CNT and graphene, as a function of temperature and starting adsorption angles (see text for details).

T	CNT/3-PEEK			CNT/6-PEEK			CNT/9-PEEK			Gr/3-PEEK	Gr/6-PEEK	Gr/9-PEEK
	$\theta = 0^\circ$	45°	90°	0°	45°	90°	0°	45°	90°	45°	45°	45°
100 K	-2.06	-1.44	-1.33	-3.35	-4.06	-5.09	-5.48	-4.56	-6.47	-4.88	-7.13	-8.70
300 K	-1.22	-1.36	-2.15	-3.20	-3.84	-5.99	-3.98	-4.49	-6.65	-2.18	-5.37	-9.26
500 K	-1.25	-1.40	-1.28	-2.89	-3.16	-4.32	-3.87	-3.59	-5.21	-2.21	-5.78	-7.80

Fig. S5 of the SI. Adsorption energies are listed in Table 4, while corresponding radius of gyration graphs are plotted in Fig. S6 of the SI.

Analysis of the results reveals an appreciably larger adsorption energy of the polymers on the flat graphene sheet in comparison to the CNTs: the adsorption energies on graphene are up to 1.2 eV/monomer larger than on CNTs. However, the adsorption energy difference per monomer appears to decrease with increasing length.

Although not quite apparent from the plots of the radii of gyration of the polymers (Fig. S6 of the SI), a physical interpretation of the trend observed for the E_b values can be gained from an analysis of the radial distribution functions (for CNT substrates) and linear distribution functions (for graphene) shown in Fig. S7 of the SI. These distributions are constructed as the percentage of the atoms that falls within intervals of 0.5 Å for all radial distances (heights) from the CNTs surface (graphene plane), and are calculated as averages over all snapshots considered. A sharp peak is observed in many of the distributions at a certain distance from the substrate and the positions of the maxima are at higher distances for CNTs than graphene, indicating that for the latter a larger percentage of the oligomer's atoms are, on average, interacting at shorter distances with the substrate. We can therefore conclude that graphene appears, compared to CNTs, to be a better candidate additive to a polymer matrix if the scope is to maximize the interaction with the polymer components.

As concerns the temperature dependence of the interaction strength, a general decrease in the magnitudes of E_b (by more than 1 eV for the longer polymers) is observed at 500 K. This observation applies to all substrates including the graphene sheet and can be explained by the smaller number of polymer and substrate atoms interacting at short distances, as clearly seen in the radial distribution function plots.

A notable dependence of E_b values on the initial angle with the (8,8) CNT substrate is worth mentioning. Simulations that start out when the fully stretched polymers make an angle of 90° with respect to the CNT axis give larger E_b values (See Fig. S8 of the SI for a graphical representation) compared to the other. This effect is not visible for the shorter polymer chain but it is evident for the larger oligomers.

4. Conclusions and perspectives

DFT and REAXFF-Ig-based MD calculations were employed to study the graphene/PEEK and CNT/PEEK interfaces. This is, to the authors' knowledge, the first joint DFT and MD calculations for these particular interfaces. The Ig variant of the REAXFF force field and van der Waals corrected DFT were employed to accurately model long-range interactions. The energetics and geometry of adsorption of the three aromatic subunits of a single PEEK monomer along with the monomer itself were investigated for both graphene and CNT substrates using DFT and subsequently used to benchmark and validate the MD protocol. The adsorption strength of a single PEEK monomer varies very little with increasing radius of the CNTs and is slightly smaller on the CNT substrates than on a flat graphene sheet. Moreover, the interaction strength of the adsorbed species on zigzag and armchair CNTs are similar radii.

The dependence of PEEK adsorption energy on the polymer chain length, temperature, starting adsorption configuration of the fully stretched conformation, and on the nature of the substrate was inves-

tigated as well. The MD simulations show that, starting from a fully stretched polymer configuration, all oligomers fold, to a certain extent, depending on the nature of the substrate. Polymers on the CNTs sit, on average, farther from the substrate's surface compared to graphene, and this results in significantly larger E_b values for PEEK interaction with graphene compared to CNTs.

Some more observations on various parameters that govern the interaction strength of the polymer with the carbon nanostructures can be made: adsorption energies are lower at 500 K, suggesting that at the higher temperature conformations that maximizes intramolecular interactions compared to adsorbate-substrate interactions are preferred. There also appears to be a slight E_b dependence on the starting angle that the fully stretched polymers make with the CNTs axis. This study suggests that graphene could be used more effectively compared to CNTs in instances where CNTs/PEEK stabilizing interactions are of common use for modulating the mechanical properties of PEEK matrices, such as mechanical reinforcement.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CRediT authorship contribution statement

Gozdenur Toraman: Conceptualization, Formal analysis, Investigation, Visualization. **Elif Sert:** Conceptualization, Formal analysis, Investigation, Visualization. **Hasan Gulasik:** Conceptualization, Investigation. **Daniele Toffoli:** Investigation, Writing - original draft, Writing - review & editing. **Hande Ustunel:** Supervision, Investigation, Writing - original draft, Writing - review & editing, Project administration. **Ercan Gurses:** Supervision, Investigation, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.commsci.2021.110320>.

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