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On the Wrapping of Polyglycolide, Poly(Ethylene Oxide), and Polyketone Polymer Chains Around Single-Walled Carbon Nanotubes Using Molecular Dynamics Simulations

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Abstract By using molecular dynamics simulations, the interaction between a single-walled carbon nanotube and three different polymers has been studied in this work. The effects of various parameters such as the nanotube geometry and temperature on the interaction energy and radius of gyration of polymers have been explored. By studying the snapshots of polymers along the single-walled carbon nanotube, it has been shown that 50 ps can be considered as a suitable time after which the shape of polymer chains around the nanotube remains almost unchanged. It is revealed that the effect of temperature on the interaction energy and radius of gyration of polymers in the range of 250 to 500 K is not significant. Also, it is shown that the interaction energy depends on the nanotube diameter.

Keywords Nanocomposites · Polymer · Single-walled carbon nanotube · Wrapping · Molecular dynamics simulation

1 Introduction

Recently, the applications of carbon nanotubes (CNTs) to reinforce polymer matrix nanocomposites have received great interest. This is because of the enhancement of mechanical [1], thermal [2], optical [3], electrical, and magnetic [4] properties of polymer by adding

CNTs to this type of nanocomposites. To increase the interfacial bonding of CNT–polymer nanocomposites, CNTs can be functionalized to have a covalent bonding between CNTs and polymers [5–7]; however, this can adversely affect some mechanical properties [8, 9]. So, noncovalent bonding, wrapping, of polymer chains around CNTs to improve the mechanical properties is of great importance [10].

Due to difficulty of experimental investigations on the CNT–polymer interface, the molecular dynamics (MD) simulations have been used. Liao and Li [11] studied the interfacial characteristics of a CNT-reinforced polystyrene (PS) nanocomposite system through molecular mechanics simulations and elasticity calculations. They reported that nonbond interactions contribute to the interfacial stress transfer ability. Gou et al. [12] used a combination of computational and experimental methods to study the interfacial bonding of single-walled carbon nanotube (SWCNT)-reinforced epoxy composites. Using force-field-based MD, Yang et al. [13] studied the interaction between polymers and CNTs.

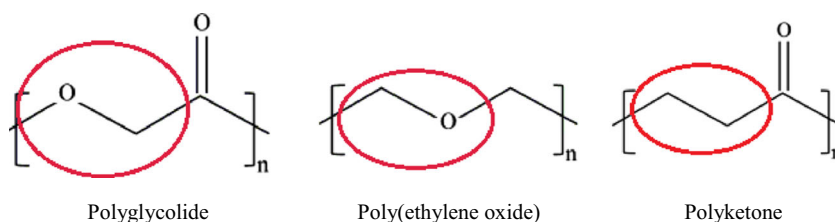
Xie and Soh [14] performed MD simulations on the complex amylose–nanotube system to study the mode of interaction between the initially separated amylose and SWCNT fragments. Wei [15] showed that depending on atomic structures of CNT, lattice and geometric coiling energy polyethylene (PE) molecules have selective conformations on CNT surface. Liu et al. [16] used MD simulations based on COMPASS to study the interactions between polymers and SWCNTs.

Caddeo et al. [17] studied the adhesion of poly(3-hexylthiophene) on SWCNTs via MD simulations. Employing position restrained (PR) MD simulations, Wu [18] investigated the bulk models for the two composite systems including epoxy monomers and CNTs. Minoia et al. [19] characterized the morphological and

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Fig. 1 Repeat units of used polymers (a *circle* is plotted around the bond used to trace their dihedral angles)



energetic properties of PE/carbon nanotubes by MD simulations. They found a regular lamellar-type formation for the adsorbed PE chain on the nanotube surface. Rouhi et al. [20] used MD simulations to investigate the adsorption of poly(phenylacetylene), PS sulfonate, and polyvinyl pyrrolidone on SWCNTs. It was shown that the time of 20 ps can be considered as the adsorption time of the polymer chains on SWCNTs.

Herein, MD simulations have been conducted to study the interaction between SWCNTs and three different polymers, including polyglycolide, poly(ethylene oxide), and polyketone. The adsorption of these polymers on the SWCNTs surface has been investigated. Besides, the effects of different parameters such as the CNT geometry and temperature on the interaction energy and radius of gyration have been examined. The snapshots of the wrapping process of polymer chains at different times have been plotted.

2 Molecular Model

Three different polymers have been chosen for the analysis whose repeat units can be seen in Fig. 1. Compared to chains considered in Rouhi et al. [20], the chains under the present study have no rings in their repeat units. So, they are more flexible. Besides, due to the presence of O atoms in the repeat units of all chains, the effect of O atom position on the polymer/SWCNT interactions can be studied in the present article. A summary of polymer chains information is given in Table 1. As it can be seen, almost equal numbers of atoms have been selected to have comparable results. Moreover, different armchair and zigzag SWCNTs have been used for the analysis, whose information is given in Table 2. It should be noted that

Table 1 Series of polymers used

Polymer name	Number of repeat units	Number of atoms
Polyglycolide	33	200
Poly(ethylene oxide)	28	198
Polyketone	24	194

the lengths of all armchair and zigzag nanotubes are 101.571 Å and 102.24 Å, respectively. Furthermore, hydrogen atoms have been added to both ends of nanotubes to avoid the unsaturated boundary effect.

3 Force Field

The adaptive intermolecular reactive empirical bond-order (AIREBO) potential function [21] is used to model the interaction between carbon and hydrogen atoms in SWCNT. Also, the AMBER force field is used to simulate the interatomic interactions in polymer chains [22]. The interactions between atoms of polymer chains and nanotubes are characterized using the Lennard-Jones potential function [23].

4 Simulation Method

The LAMMPS MD code [24, 25] has been used to perform MD simulations. All of the simulations have been done under a constant number of molecules, constant volume, and constant temperature (NVT) conditions. A period of 50 ps has been used to equilibrate the simulation system, and after that, the interactions have been recorded for 250 ps. The time step for both of the stages has been selected as 1 fs. The potential energy variation of a system containing the utilized polymer chains at the side of a (11,11) SWCNT has been represented in Fig. 2.

5 Results

5.1 Wrapping Process

In each case, four different initial angles, between polymer chain and SWCNT axis, were selected including 0° , 30° , 60° , and 90° . The initial configurations of polymer chains and a (11,11) armchair SWCNT with the initial angle of 0° have been shown in Fig. 3. Also in this figure, the snapshots of polymers along the SWCNT have been shown at different time steps. The blue, gray,

Table 2 Properties of the SWCNTs used

Armchair				Zigzag			
Chirality	Diameter (Å)	Number of C atoms	Number of H atoms	Chirality	Diameter (Å)	Number of C atoms	Number of H atoms
(8,8)	10.85	1,312	32	(14,0)	10.96	1,344	28
(11,11)	14.92	1,804	44	(19,0)	14.87	1,824	38
(15,15)	20.34	2,460	60	(26,0)	20.36	2,496	52
(20,20)	27.12	3,280	80	(35,0)	27.4	3,360	70

and red colors have been employed to show the C, H, and O atoms, respectively. As it can be seen, for all polymers, 50 ps can be considered as the adsorption time after which the shape of polymers would not change significantly. After 50 ps, the chains wraps around the diameter and along the length of the nanotube, and their shape would not change remarkably. For comparison, the configuration of the system has been shown at 100 ps.

5.2 Interaction Energy

To study the dynamic behavior of polymer chains, the interaction energy of the polymer–nanotube systems is obtained as follows:

$$E_{\text{inter}} = E_{\text{polymer-CNT}} - (E_{\text{polymer}} + E_{\text{CNT}}) \quad (1)$$

in which E_{inter} is the interaction energy and $E_{\text{polymer-CNT}}$, E_{polymer} , and E_{CNT} are the potential energies of polymer–nanotube system, polymer, and nanotube, respectively.

In Figs. 4 and 5, total interaction energy and interaction energy per nonhydrogen atoms of the polymer chains have been plotted against the nanotube diameter

for armchair and zigzag nanotubes. It should be noted that in all of the figures associated with interaction energies, the averaged energies for four different initial configurations are plotted. The polyglycolide, poly(ethylene oxide), and polyketone polymer chains have, respectively, 132, 84, and 96 nonhydrogen atoms, respectively. As it can be seen, increasing the nanotube diameter results in increasing the interaction energy. This can be related to the larger surface area of the nanotubes with larger radii which leads to more interaction between atoms of polymer chains and SWCNTs. Moreover, larger nanotubes contain more atoms that can interact with polymer chains which leads to increasing interaction energy. Furthermore, it can be seen that except in the initial part of figures, the interaction energy of polyglycolide–nanotube system is larger than that of other systems, next to polyketone–nanotubes and then poly(ethylene oxide)–nanotubes. By comparing these figures with Fig. 1, it can be said that locating O atoms at the sides of chains results in larger interaction energy. So, the polyketone–SWCNT interaction is more powerful than that of poly(ethylene oxide)–SWCNTs. Polyglycolide has O atoms in both backbone and side of backbone. So, it possesses the largest interaction energy. Besides, as it can be seen in the interaction energy per nonhydrogen atoms, the energy of poly(ethylene oxide)/SWCNT is the largest energy and that of polyglycolide /SWCNT is the lowest one. So, another reason for larger interaction energy of polyglycolide can be its more nonhydrogen atoms.

The effect of temperature on the total interaction energy and interaction energy per nonhydrogen atoms has been investigated in Fig. 6. Here, all of the chains have been studied around a (19,0) nanotube. With the step of 25 K, the range of 250 to 500 K has been studied. As it can be observed, although there are some ups and downs in the interaction energies, the effect of temperature on the interaction energy is weak especially for poly(ethylene oxide) and polyketone polymer chains. This can be attributed to the powerful interactions between nanotube and polymer chains in the used temperature range.

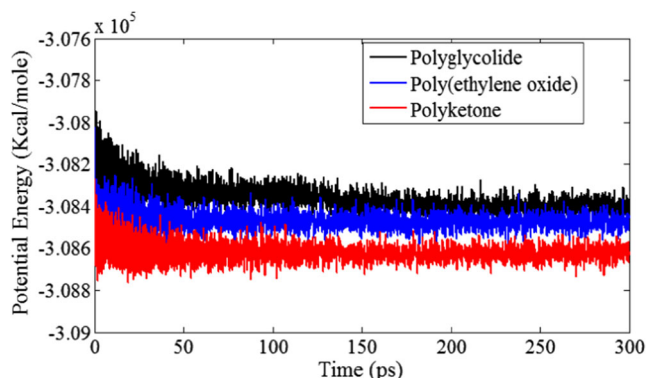


Fig. 2 The potential energy variation of a system containing the utilized polymer chains at the side of a (11,11) SWCNT

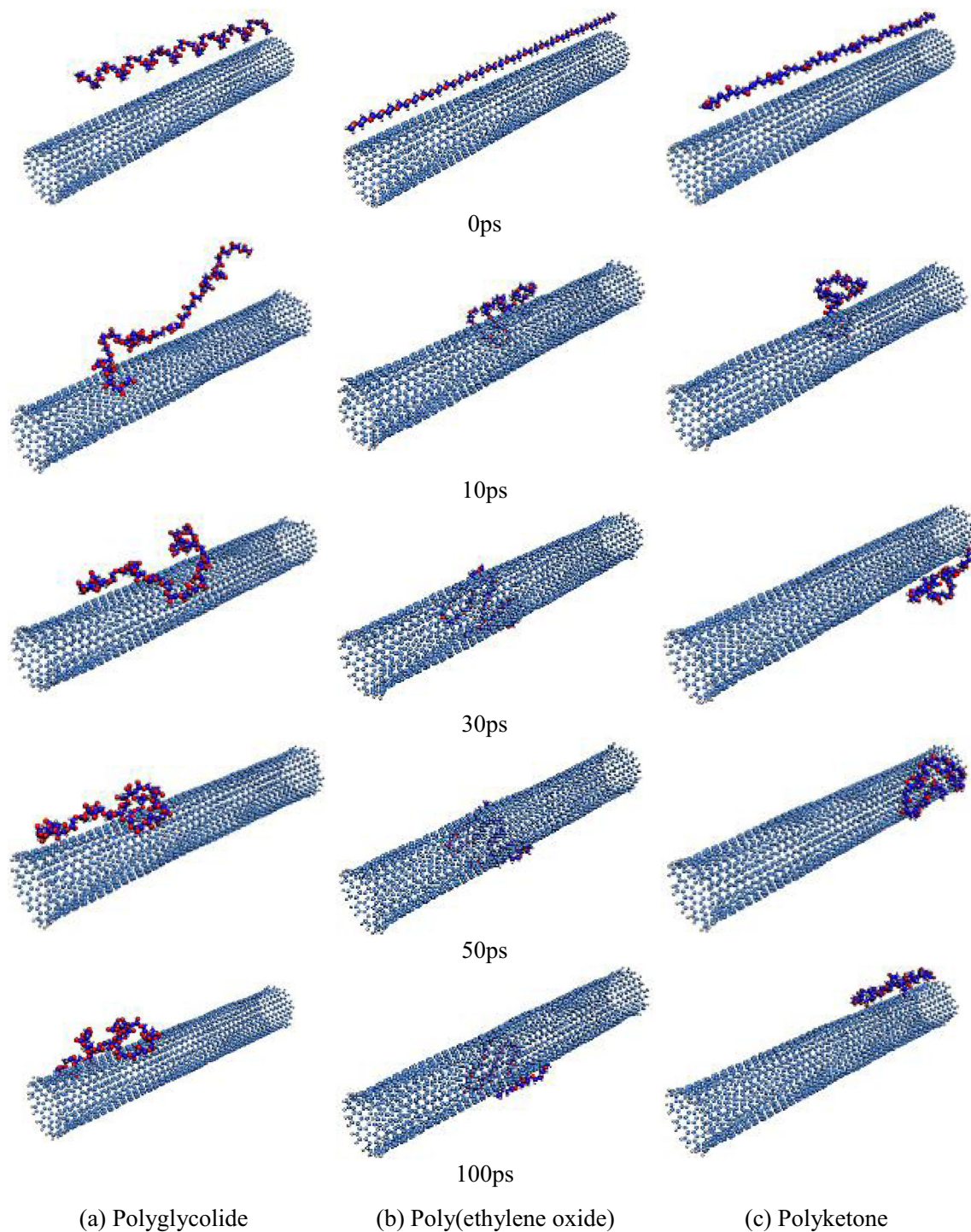


Fig. 3 Snapshots of polymer chains along the SWCNT at different time steps. **a** Polyglycolide. **b** Poly(ethylene oxide). **c** Polyketone

5.3 Radius of Gyration

The radius of gyration, which is used to define the overall size of the polymer chain, can be expressed as follows:

$$R_g = \left(\frac{1}{N} \left(\sum_{i=1}^N (r_i - r_{cm})^2 \right) \right)^{1/2} \quad (2)$$

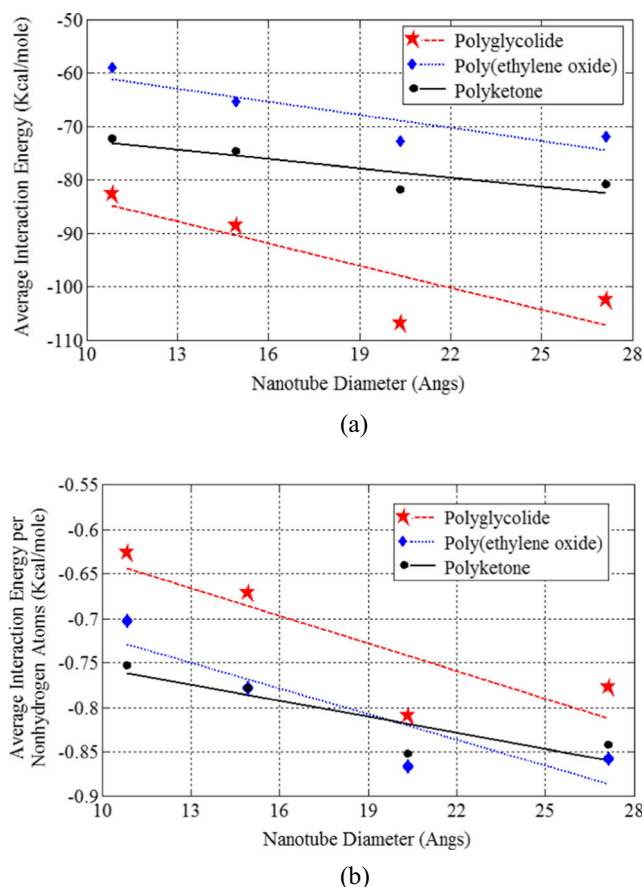


Fig. 4 **a** Total interaction energy and **b** interaction energy per nonhydrogen atoms of polymer chains wrapped around the armchair nanotubes versus the nanotube diameter

in which r_i and r_{cm} are the position vector of each atom and center of mass of polymer chain, respectively, and N is the number of atoms of polymer chain. The time variation of R_g of polymer chains around a (11,11) SWCNT has been plotted in Fig. 7. It is found that radius of variation decreases during simulation. It means that the polymer chains collapse during the time. The time variations of sample dihedral angles (for the bonds shown in Fig. 1) for each of the polymer chains are given in Fig. 8.

As it is seen in Fig. 2, after 150 ps, the potential energy of all chains oscillates around a constant value. So, this time can be considered as the time at which systems reach to their stable condition. Besides, in Fig. 7, for all three types of chains, after 150 ps, the R_g remains almost unchanged. In Fig. 8, again, it is observed that after 150 ps, the variation of dihedral angle for all type of chains is small. Thus,

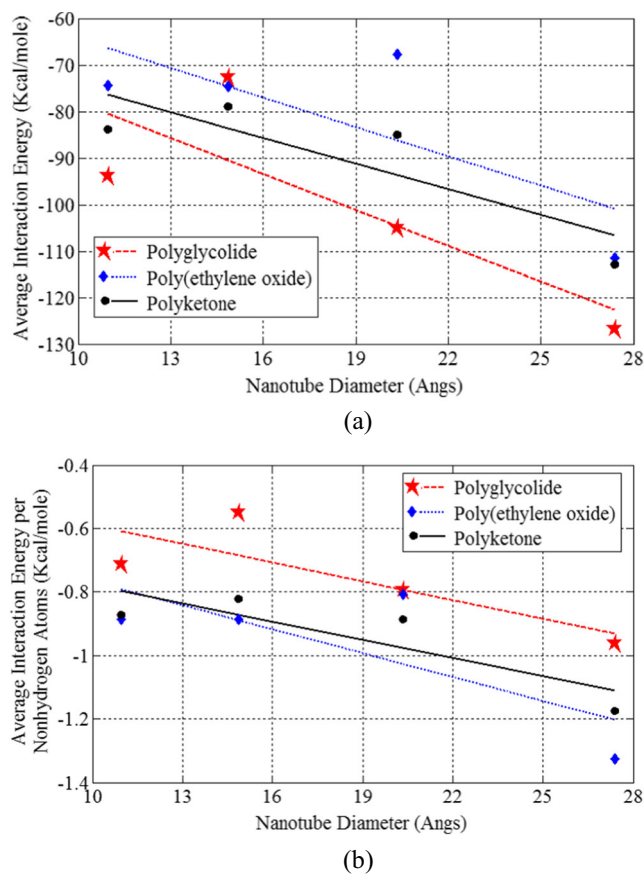
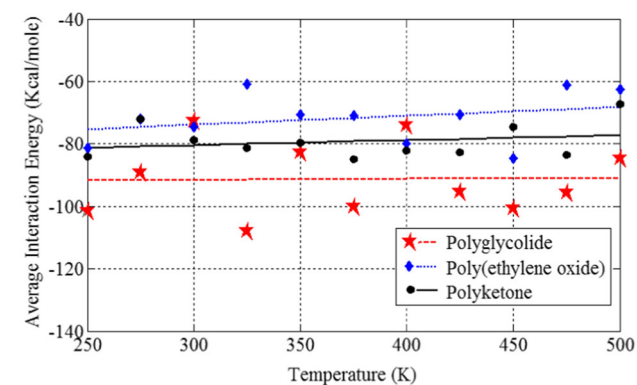


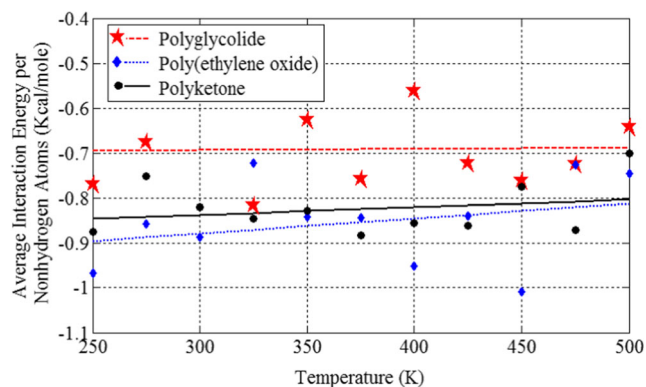
Fig. 5 **a** Total interaction energy and **b** interaction energy per nonhydrogen atoms of polymer chains wrapped around the zigzag nanotubes versus the nanotube diameter

from Figs. 2, 7, and 8, one can conclude that after 150 ps, the chains can be considered stable and the employed simulation time is enough. This time is longer than the time obtained for the stiffer chains studied in Rouhi et al. [20]. So, one can conclude that the more flexibility the chains have, the longer the time they need to reach the stability in the interactions with SWCNTs.

The radii of gyration of polymer chains wrapped around armchair and zigzag nanotubes have been plotted against nanotube diameter in Figs. 9 and 10. According to these figures, all polymer chains experience reduction by increasing the SWCNT diameter. This means that chains have more extended forms at the side of SWCNTs with smaller radii. The values of R_g are associated with the polyglycolide, then polyketone and after that poly(ethylene oxide).



(a)



(b)

Fig. 6 **a** Total interaction energy and **b** interaction energy per nonhydrogen atoms of polymer chains wrapped around a (19,0) nanotube versus temperature

The effect of temperature on the radius of gyration has been investigated in Fig. 11. The results are similar to the effect of temperature on the interaction energy, which means that in spite of some fluctuations, the effect of temperature on R_g is not predominant.

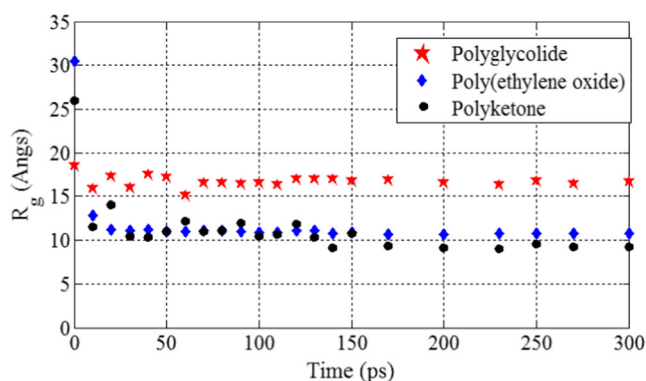


Fig. 7 Variation of radius of gyration with the simulation time

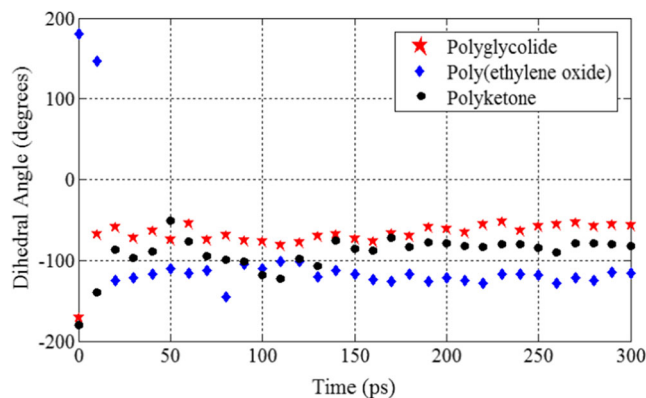


Fig. 8 Variation of a sample dihedral angle with the simulation time

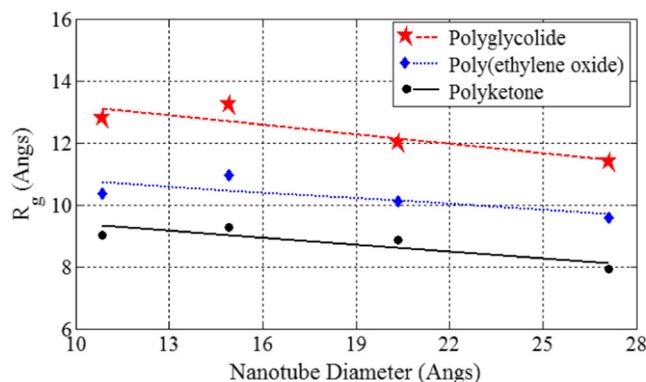


Fig. 9 Radius of gyration of polymer chains wrapped around the arm-chair nanotubes versus the nanotube diameter

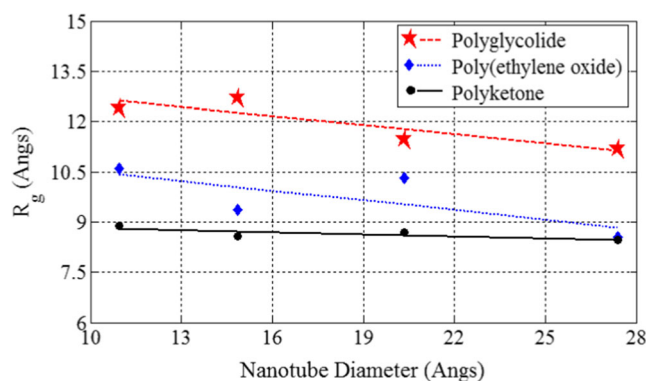


Fig. 10 Radius of gyration of polymer chains wrapped around the zigzag nanotubes versus the nanotube diameter

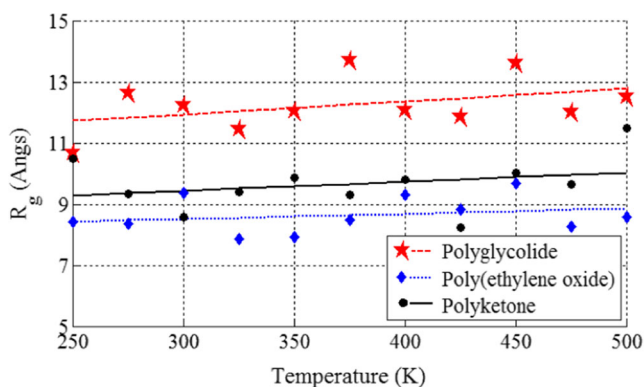


Fig. 11 Radius of gyration of polymer chains wrapped around a (19,0) nanotube versus temperature

5.4 x - θ Profile of the Adsorbed Chains

The final conformations of the atoms located on the backbone of polymer chains are given in Figs. 12, 13,

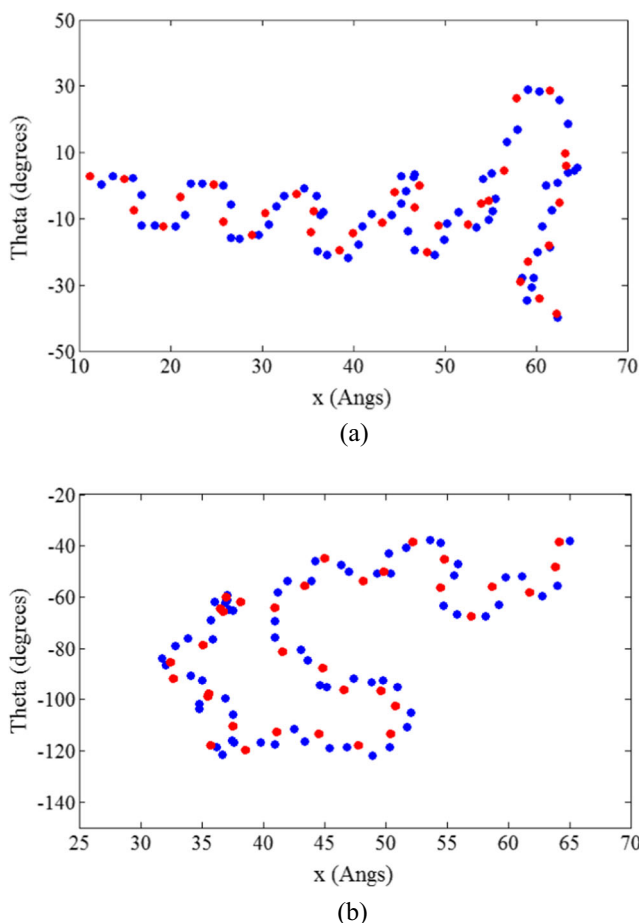


Fig. 12 x - θ profile of a polyglycolide chain adsorbed on **a** (11,11) and **b** (19,0) SWCNTs

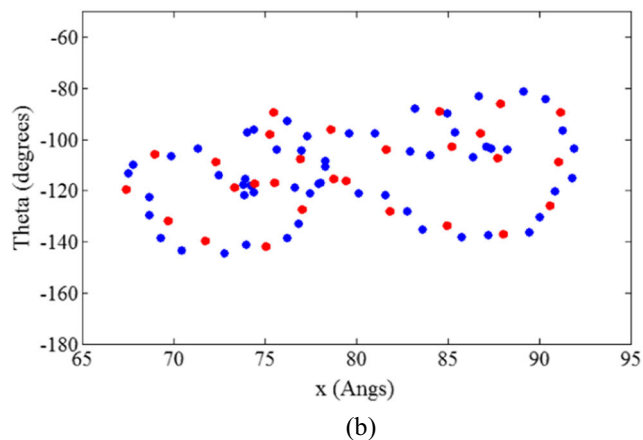
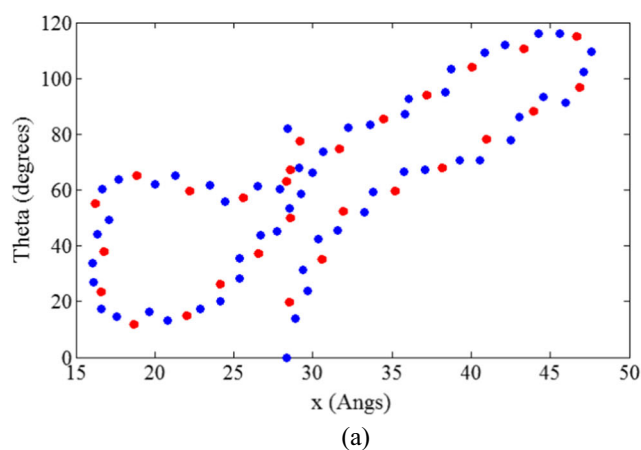


Fig. 13 x - θ profile of a poly(ethylene oxide) chain adsorbed on **a** (11,11) and **b** (19,0) SWCNTs

and 14 at the side of two sample SWCNTs. In these figures, x -axis shows the longitudinal position along the SWCNT axis. The origin of x -axis is located at the left corner of the SWCNT. Besides, the y -axis shows the circumferential coordinates of polymer chain atoms. This coordinate can be used to study the extension state of polymer atoms around the SWCNT.

It should be noted that blue and red atoms show C and O atoms, respectively. It is seen that while polyglycolide and polyketone chains have nonlinear shapes at the side of both of the nanotubes, poly(ethylene oxide) has a linear shape. These behaviors can be attributed to the structure of chain monomers that were shown in Fig. 1. Poly(ethylene oxide) has no nonhydrogen atoms other than the atoms located on its backbone. However, other chains have O atoms which lead to their nonlinear shapes.

The final positions of polymer atoms relative to a (11,11) SWCNT are given in Fig. 15. It is seen that the

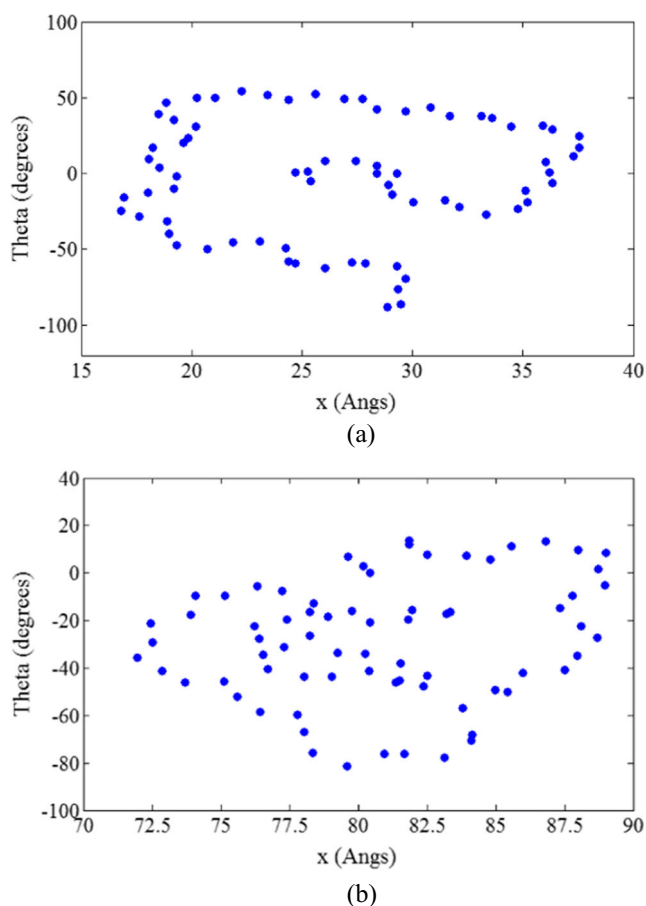
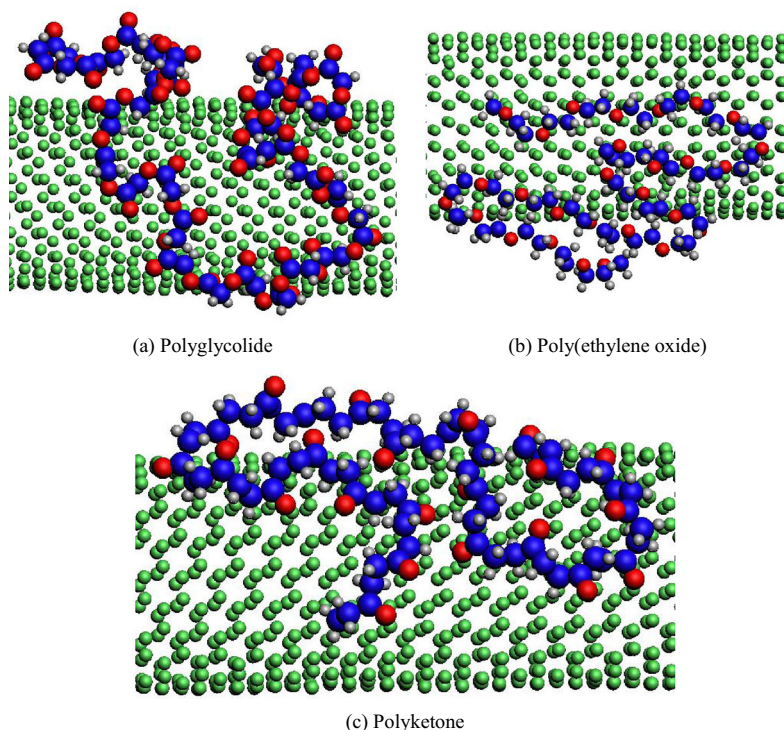


Fig. 14 $x-\theta$ profile of a polyketone chain adsorbed on **a** (11,11) and **b** (19,0) SWCNTs

Fig. 15 Conformations of the polymer atoms relative to SWCNT. **a** Polyglycolide. **b** Poly(ethylene oxide). **c** Polyketone



atoms of polymer chains try to locate at the top of SWCNT atoms, so that their bond can be directed along the hexagon sides. However, due to compact arrangements, some atoms are located at the top of hexagons over empty places.

6 Concluding Remarks

MD simulations were conducted to investigate the interaction between SWCNTs and polymer chains. The wrapping of three different polymer chains around the SWCNTs with different chiralities and diameters was studied. Furthermore, the effect of temperature on the interaction between polymer chains and SWCNT was explored. It was shown that after 50 ps from the beginning of simulation, the shape of polymer chains around the nanotube would not change significantly. Besides, after this time, the radius of gyration of all the polymer chains converges to a constant value after which, although the chains move around the SWCNT and along it, the radius of gyration would not change significantly. It was shown that by increasing the nanotube diameter, the interaction energy increases. In addition, the interaction energy of polyglycolide–nanotube system is larger than that of the other systems. The system of polymer chains and SWCNT was considered in the range of 250 to 500 K to study the effect of temperature on the wrapping process, and it was shown that generally in the range of investigation, the effect is not predominant.

References

1. R. Sen, B. Zhao, D. Perea, M.E. Itkis, H. Hu, J. Love, E. Bekyarova, R.C. Haddon, *Nano Lett.* **4**, 459–464 (2004)
2. T.C. Clancy, T.S. Gates, *Polymer* **47**, 5990–5996 (2006)
3. E. Kymakis, G.A.J. Amaratunga, *Appl. Phys. Lett.* **80**, 112–115 (2002)
4. J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, *Polymer* **44**, 5893–5899 (2003)
5. Q. Zheng, D. Xia, Q. Xue, K. Yan, X. Gao, Q. Li, *Appl. Surf. Sci.* **255**, 3534–3543 (2009)
6. N.G. Sahoo, S. Rana, J.W. Cho, L. Li, S.H. Chan, *Progr. Polym. Sci.* **35**, 837–867 (2010)
7. M.M. Rahmana, S. Zainuddin, M.V. Hosur, J.E. Malone, M.B.A. Salama, A. Kumar, S. Jeelani, *Composit. Struct.* **94**, 2397–2406 (2012)
8. M. Wong, M. Paramsothy, X.J. Xu, Y. Ren, S. Li, K. Liao, *Polymer* **44**, 7757–7764 (2003)
9. C. Xu, Z. Jia, D. Wu, Q. Han, T. Meek, *J. Electron. Mater.* **35**, 954–957 (2006)
10. D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **106**, 1105–1136 (2006)
11. K. Liao, S. Li, *Appl. Phys. Lett.* **79**, 4225–4227 (2001)
12. J. Gou, B. Minaie, B. Wang, Z. Liang, C. Zhang, *Comput. Mater. Sci.* **31**, 225–236 (2004)
13. M. Yang, V. Koutsos, M. Zaiser, *J. Phys. Chem. B* **109**, 10009–10014 (2005)
14. Y.H. Xie, A.K. Soh, *Mater. Lett.* **59**, 971–975 (2005)
15. C. Wei, *Nano Lett.* **6**, 1627–1631 (2006)
16. W. Liu, C.L. Yang, Y.T. Zhu, M.S. Wang, *J. Phys. Chem. C* **112**, 1803–1811 (2008)
17. C. Caddeo, C. Melis, L. Colombo, A. Mattoni, *J. Phys. Chem. C* **114**, 21109–21113 (2010)
18. C. Wu, *J. Polymer, Sci. Part B: Polymer Phys.* **49**, 1123–1130 (2011)
19. A. Minoia, L. Chen, D. Beljonne, R. Lazzaroni, *Polymer* **53**, 5480–5490 (2012)
20. Y. Rouhi, R. Alizadeh, Ansari, *Fibers and Polymers* **15**, 1123–1128 (2014)
21. D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, N.B. Boris, S.B. Sinnott, *J. Phys. Condens. Matter* **14**, 783–802 (2002)
22. W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, P.A. Kollman, *J. Am. Chem. Soc.* **117**, 5179–5197 (1995)
23. J.E. Jones, *Proc. R. Soc. Lond. A.* **106**, 463–477 (1924)
24. LAMMPS Molecular Dynamics Simulator. <http://lammps.sandia.gov>
25. S. Plimpton, *J. Comput. Phys.* **117**, 1–19 (1995)