Adsorption of polyethylene, polypropylene, polyvinyl chloride monomer units on the single-walled carbon nanotube surface

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Received 10 October 2014, www.cmnt.lv

Abstract

The paper presents the results of research into the interaction mechanism between single-walled carbon nanotubes and most common polymers that results in the formation of stable polymer based nanotube reinforced composites. Nanotubes used as reinforcement provide strong as well as plastic polymer based nanocomposites that have a promising field of commercial application. The main characteristics of the interaction process between the nanotube (6, 6) and monomers of the polymers under study are defined. Calculations are performed by applying DFT method and B3LYP functional.

Keywords: carbon nanotubes, polyethylene, polypropylene, polyvinyl chloride, adsorptive interactions, polymer based nanocomposites, reinforcement, density functional theory method

1 Introduction

One of the most important fields in polymer technology offering promising results is the development of polymer based nanocomposites that are produced by modifying the polymer matrix structure with various nanoparticles (carbon nanotubes, fullerenes [1-5]). It is reported that these nanosized fillers change the polymer matrix structure and have the potential to enhance its operational and other properties [6]. Of the various nanofillers used to modify polymer matrices, carbon nanotubes have attracted great interest recently as structural reinforcements because of their unique properties. Reports show that composites filled with carbon nanotubes (CNTs) displayed an increase in strain before breakdown as compared to the original pure polymer (for epoxy based composites the effect is described in [7], for phenylon [8]). Small amounts of CNTs (0.1-2 %) added to the polymer structure increase both the elastic modulus and tensile strength of the polymer manifold [9, 10]. Simultaneously, thermal and electrical conductivity of the composite showed a considerable increase. The paper [10] reported the fabrication of a polymer composite composed of a large number of vertically arranged multi- walled carbon nanotubes where the space between the layers was filled with polydimethylsiloxane. Research showed that a cyclic load on the polymer did not cause mechanical fatigue and led to the composite hardening.

The major drawback of polymer composites is a gradual decrease in elasticity with an increasing amount of filler content, all polymer composites modified with CNTs show a significant elasticity enhancement, and this effect is important for practical application. However, the interaction mechanism between polymers and carbon nanotubes contributing to improvements in plasticity, elasticity and hardening of nanocomposites has not been studied so far.

In this paper, we present the study of the interaction mechanism between single-walled carbon nanotubes and the most common polymers - polyethylene, polypropylene and polyvinyl chloride. Taking into consideration the atomic and electronic structure of CNTs that is characterized by the presence of non-zero curvature of the surface that results in non-orthogonality of σ and π- bonds, we believe it is possible to implement adsorption of polymers on the nanotube surface. This process will lead to the formation of stable polymer-based composites reinforced with CNTs having enhanced strength and plasticity.

We performed quantum-chemical calculations of the interaction process between polyethylene, polypropylene and PVC monomers and single-walled carbon nanotubes of «arm-chair» type (n, n) that have cylindrical symmetry. Calculations were performed by using the density functional method (DFT) and B3LYP functional [11].

2 Study of polyetilene adsorption mechanism on the single-walled nanotube surface (6,6)

The possibility for the monomer ethylene $CH_2=CH_2$ to bind to the single-walled carbon nanotube (6, 6) external surface was investigated. Molecular clusters (MC) containing six hexagon cycles on the tube perimeter and four elementary layers along the tube axis were selected as a geometric model of the tubulene. Since a nanotube is an infinite structure hydrogen pseudo atoms were used to complete loose chemical bonds on the nanotube edge. The interaction model between tubulene (6, 6) and ethylene monomer is shown in Figure 1. The interaction takes place via one of the possible adsorption centers of ethylene: a – the monomer hydrogen atom when as a result of interaction C – H bond is formed; b – the monomer carbon atom when as a result of interaction C – C bond is formed. To avoid the boundary effects the position for the adsorbed monomer was chosen approximately in the middle of the nanotube cluster.

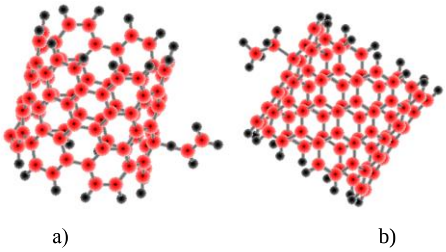
a) b)

FIGURE 1 The interaction model between the ethylene monomer and carbon nanotube (6, 6): a) adsorption via the H centre of ethylene with C – H bond formation; b) adsorption via the C centre of ethylene with C – C bond formation

The adsorption process for the *polyethylene* molecule on the selected atom on the nanotube external surface was modeled in increments of 0,01 Å. Optimization of the system geometry was performed incrementally and as a result the potential energy curves of the adsorption process were calculated (Figure 2).

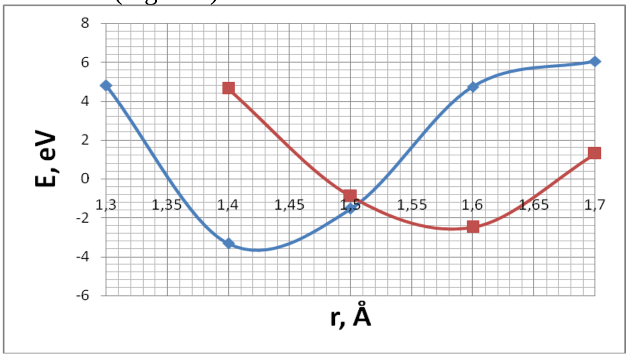

FIGURE 2 The energy curves of the ethylene molecule adsorption process on the nanotube external surface via the H adsorption center of ethylene with the C – H bond formation (the blue line) and via the center C adsorption center of ethylene with C – C bond formation (the red line)

Analysis of the adsorption complex geometry optimization results found that the cylindrical symmetry of the tube is broken due to an increase in length of the C–C bond in the carbon hexagon when the ethylene molecule is adsorbed on the C atom. An average elongation is 5 % of the original **C – C *bond*** length that is equal to 1,4 Å. Values of interaction energies were calculated as the difference between the total energy of the non-interacting adsorbent (in this case, the carbon nanotube plus ethylene monomer) and the one of the adsorption complex: $E_{ad} = E_{ad.c.} – (E_{tub} + E_{eth})$.

Analysis of the results showed that the interaction process is implemented, which is illustrated by the presence of a minimum on the energy curves (Fig. 2). Basic parameters for variants (a) and (b) of the adsorption interaction are shown in Table 1.

TABLE 1 The main characteristics of the interaction process between carbon nanotube (6, 6) and polyethylene, polypropylene and polyvinyl chloride monomers for different variants: a - via hydrogen atom of the monomer with C – H bond formation, b - via a carbon atom of the monomer with C – C bond formation; r_{ad} – adsorption distance, E_{ad} - adsorption energy.

Interaction variants	a, C-H bond		b, C-C bond	
	r_{ad}, Å	E_{ad}, eV	r_{ad}, Å	E_{ad}, eV
Polyethylene	1, 42	-3,83	1,59	-2,48
Polypropylene	1,8	-6,64	1,5	-5,43
Polyvinyl chloride	2,5	-8,41	2,1	-1,98

Thus, calculations revealed that for both variants of interaction (a – C–H bond, b – C – C bond) adsorption is possible. Meanwhile, it was found that energetically more favorable interaction with the carbon nanotube takes place via the hydrogen atom adsorption center with C– H bond formation (the adsorption energy value in this case is larger than in the case of (b), ΔE = 1,35 eV). The fact that chemical interaction takes place at a sufficiently small distance proves that there is a strong bond between CNT and polyethylene fragment. Thus, it can be assumed that CNTs can form the so-called reinforcement for polyethylene polymer matrix that provides strength of the polymer composite.

3 Study of polypropylene monomer adsorption mechanism on the single-walled nanotube surface (6,6)

The possibility of monomer CH_2=CH-CH_3 polypropylene-CH3 to bind to the external surface of single-walled carbon nanotube (6, 6) was investigated. The interaction model was similar to the one described in the previous section for CNTs and ethylene monomer. Interaction is carried out through one of the propylene molecule adsorption centers: a – hydrogen atom of the monomer, b - a carbon atom of the monomer (Figure 3).

As a result of incremental calculations the energy curves of the adsorption process for the two variants of the interaction process were built, that are shown in Fig. 4. Each of the curves has a minimum which indicates the presence of adsorption interaction systems. It is obvious that interaction via a hydrogen atom of propylene is energetically more favorable. The curve analysis for the variant where adsorption takes place via C atom of the propylene molecule revealed that the curve has two minima.

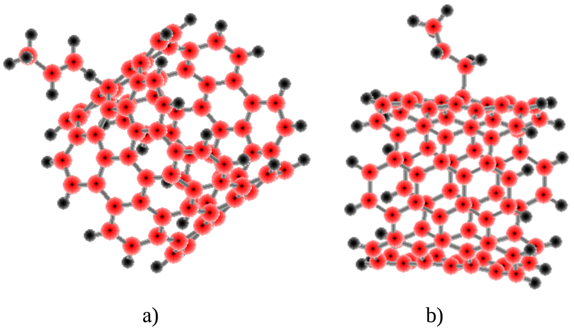
a) b)

FIGURE 3 The interaction model between propylene monomer and carbon nanotube (6, 6): a) adsorption via H center of ethylene with C – H bond formation; b) adsorption via C center of ethylene with C – C bond formation

It means that in order to reach a second minimum at a distance of 1,52 Å, the propylene molecule has to overcome a small potential barrier height of 2.8 eV. The second minimum is energetically more favourable ($E_{ad(II)}$ = -5,8 eV), that is why this state of the adsorption complex is more stable as compared to the one that is formed when the propylene molecule is located at a distance of 1,89 Å, where $E_{ad(I)}$ = -1,2 eV. The main parameters of the process are given in Table 1.

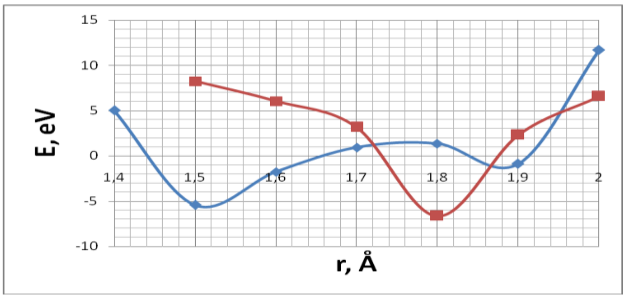

FIGURE 4 The energy curves of the propylene molecule adsorption on the external surface of the nanotube via the H adsorption center H of propylene with C –C bond formation (the blue line) and via the C center of ethylene with the C – H bond formation(the red line)

Thus, the results of the study proved the possibility of adsorption interaction between carbon nanotube and polypropylene monomer. This allows us to assume that the reinforcement of the polymer matrix with small diameter carbon nanotubes will provide useful properties of polymer composites promising for practical application.

4 The adsorption mechanism of polyvinyl chloride monomer on the single-walled nanotube surface (6,6)

Further, the possibility for polyvinyl monomer - CH2-CH-Cl- to bind to the external surface of single-walled carbon nanotube (6, 6) was investigated. As in previous cases, molecular clusters containing six hexahydric carbon cycles (hexagons) around the tube perimeter and four elementary layers along the tube axis were selected to serve as a geometric model of the tubulene. The cluster boundaries were completed by pseudo hydrogen atoms. The interaction was modeled via one of the adsorption centers of polyvinyl chloride (PVC) monomer: A – the hydrogen atom of the monomer, b - the carbon atom of the monomer. To eliminate the boundary effects the position of the adsorbed monomer was taken to be in the middle of the nanotube cluster.

The adsorption process of PVC monomer on the carbon nanotube external surface was modeled in increments of 0,01 Å and accompanied by full optimization of the geometrical structure of the interacting systems. The calculations of the energy curves constructed for the interaction process are shown in Fig. 5. The presence of minimum on the curves indicates adsorption interaction of the systems. It was found that energetically more favorable type of interaction takes place via a hydrogen atom of PVC monomer. However, in contrast to the previously considered cases where chemical interaction between CNTs and polyethylene and polypropylene monomers was observed, long adsorption distances for the PVC monomer and CNTs interaction reveal that physical adsorption is implemented, which indicates a weaker interaction between the carbon nanotube and polyvinyl chloride matrix. In this case, the most active monomer center is a hydrogen atom.

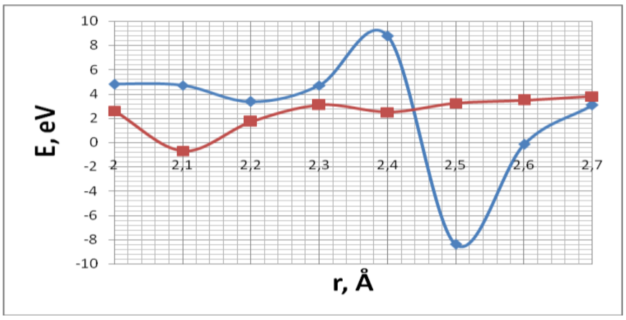

FIGURE 5 The energy curves of the interaction process between monomer polyvinyl chloride ethylene and the external surface of the nanotubes via H adsorption center of the monomer with C – H bond formation (the blue line) and via C adsorption center of the monomer with C-- C bond formation (the red line)

Analysis of single-electron spectra for all the considered interaction types found that the main contribution to the valence band of the obtained composite polymer systems is made by s- and p-orbitals of carbon atoms and s-orbital of the hydrogen atom of the selected polymers. For PVC monomer based composite s-and p-orbitals of the chlorine atom also contribute to the valence band. The conductivity band is formed by 2p atomic orbitals of carbon nanotubes in all the cases under study.

5 Conclusions

The studies of interactions between carbon nanotubes of small diameter and monomers of most common polymers of polyethylene, polypropylene and polyvinyl chloride showed that adsorption on the active centers of the monomers (C and H atoms) is possible. It was found that for all the selected polymers the interaction of the carbon nanotube and the polymer molecule via a hydrogen atom that is followed by a C-H bond formation is energetically more favorable. The calculations revealed that for interactions of the CNT and the monomers of polyethylene and polypropylene chemical interaction is realized providing a strong bond between the nanotube and polymer matrix. In contrast, "CNT – PVC" complex revealed the emergence of a weaker (in terms of energy) physical adsorption. It is concluded that CNTs may form the so-called reinforced frame of the polyethylene and polypropylene polymer matrix that provides the strength of the obtained polymer composite, which is very valuable for practical application.

References

[1] Saito R, Dresselhaus M S, Dresselhaus G 2009 *Physical properties of carbon nanotubes* Imperial London: College Press 251p

[2] Harris P J F 1999 *Carbon nanotubes and related structures. New Materials for the Twenty-first Century* New York: Cambridge University Press 336 p

[3] Zaporotskova I V 2009 *Carbon and non-carbon nanomaterials and composite structures on its base: morphology and electron properties* Volgograd:Volgograd University Press 456 p

[4] Dresselhaus M S, Dresselhaus G, Avouris P 2000 *Carbon nanotubes: synthesis, structure, properties, and application* Berlin: Springer-Verlag 464 p

[5] D'yachkov P N 2010 Electron properties and application of carbon nanotube, Moscow : BINOM 488 p

[6] Wang C, Guo Z-X, Fu S, Wu W, Zhu D 2004 Polymers containing fullerene or carbon nanotube structures *Prog. Polym. Sci.* **29** 1079–141

[7] Khabashesku V N, Barrera E V, Lobo M R F 2007 *Current Research on Nanotechnology* **1**(2) 165-82

[8] Janovskij Ju G, Kozlov G V, Burja A I, Lipatov Ju S *Fizicheskaja*

mezomehanika **10**(6) 63-7

[9] Coleman J N, Khan U, Blau W J, Gun'ko Y K 2006 Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites *Carbon* **44**(9) 1624–52

[10] Carey J B, PrabirPatra K, Ci Lijie, Glaura Silva G., and Pulickel Ajayan M 2011 Observation of Dynamic Strain Hardening in Polymer Nanocomposites *ACS Nano* **5**(4) 2715–22

[11] Koch W, Holthausen M 2002 *A Chemist's Guide to Density Functional Theory* Weinheim: Wiley-VCH. 19 p

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[2] Zaporotskova I V, Polikarpova N P, Ermakova T A, Polikarpov D I 2013 Carbon Nanotubes, New Material for Purification of Water–Ethanol Mixtures from Isomers of Propanol *Russian Journal of General Chemistry* **83**(8) 1601–6
[3] Zaporotskova I V, Anikeev N A, Kojitov L V, Davletova O A, Popkova A V 2014 Theoretical Studies of the Structure of the Metal-carbon Composites on the Base of Acryle-nitrile Nanopolimer *Journal of nano- and electronic physics* **6**(3) 03035-1 - 03035-3
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[2] Krutoyarov A A, Elbakyn L S, Zaporotskova I V 2013 About adsorption of the polyetilene monomer unit on the single-walled carbon nanotube surface *International Conference Advanced carbon Nanostructures ACNS'2013* July 01-05 2013 St-Petersburg Russia *Book of Abstracts* 2.17
[3] Krutoyarov A, Elbakyan L, Zaporotskova I V 2013 About adsorption of the polyethylene monomer unit on the single-walled corbon nanotubes surface *European Polymer Congress EPF 2013* Pisa (Italy) 16 – 21 June 2013 *Book of Abstracts* 3-6
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[2] Polikarpova N P, Vilkeeva D E, Polikarpov D I, Zaporotskova I V 2014 Sensor properties of carboxyl-modifies carbon nanotubes *Nanosystems: physics, chemistry, mathematics* **5**(1) 101-6
[3] Polikarpova N. P., Vil'keeva D. E., Zaporotskova I V 2013 Sensor Activity of Carbon Nanotubes with a Boundary Functional Group Nanoscience and Nanotechnology Letters **5**(11) 1169-73
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