M. Griebel, J. Hamaekers, R. Wildenhues

# Molecular dynamics simulations of the influence of chemical cross-links on the elastic moduli of polymer-carbon nanotube composites

# Molecular dynamics simulations of the influence of chemical cross-links on the elastic moduli of polymer-carbon nanotube composites

Michael Griebel, Jan Hamaekers, and Ralf Wildenhues

Department of Numerical Simulation, University of Bonn, Wegelerstraße 6, D-53115 Bonn, Germany.
e-mail: {griebel, hamaekers, wildenhues}@ins.uni-bonn.de

## ABSTRACT

In this article we compare the Young modulus of polyethylene carbon nanotube composites with chemical cross-links between the nanotube and the polyethylene matrix to the modulus of a composite with weak non-bonded matrix-nanotube interactions only. To this end, we employ molecular dynamics simulations using the Parrinello-Rahman approach, where all systems are modeled with a reactive many-body bond order potential due to Brenner. To analyze the effect of chemical cross-links on the Young modulus, we study systems where different amounts of carbon atoms of a capped (10,10) carbon nanotube have been cross-linked to a surrounding polyethylene matrix. Our results show that the Young modulus and thus the reinforcement of a composite material increases with the amount of cross-links.

## 1   Introduction

After their discovery by Iijima in 1991 [1], tube-like structures of pure carbon have attracted a lot of attention in the area of nanomaterial science due to their unusual material properties. In particular, carbon nanotubes possess great strength, high stability and high elasticity, but are nevertheless extremely lightweighted [2, 3]. Due to these mechanical properties, carbon nanotubes are an interesting material to be used for the reinforcement of polymer matrices. Polymer-nanotube composites possess the potential for larger strength and stiffness compared to typical carbon-fiber-reinforced polymer composites. Here, the quality of the reinforcement of the polymer matrix depends on the strength of the interactions between the nanotube and the matrix. One way to obtain relatively strong interactions is by chemical cross-linking. This is also known as functionalization [4, 5].
Meanwhile, some nanotube composites materials have been characterized experimentally [6, 7]. This however is a demanding and expensive task. To this end, numerical methods can be used to greatly facilitate the study and further development of nanotube composite materials. Here, for large systems with thousands of atoms and more, molecular dynamics calculations based on empirical potentials are an important tool to better understand macroscopic mechanical properties of composite materials [8]. In particular, molecular dynamics simulations have been successfully applied to study the mechanical properties of polyethylene nanotube composites [4, 9, 10].

In this work, we perform molecular dynamics simulations of composite systems consisting of a polyethylene matrix and an embedded carbon nanotube. We apply tensile loads, derive stress-strain curves and thus predict the Young modulus of the composite material. In particular, we examine composites with non-bonded weak interactions as well as chemical cross-links between the atoms of the nanotube and the matrix. The results of our numerical simulations show that the Young modulus and thus the reinforcement of a composite increases with the amount of cross-links.

## 2   Computational Methods

In our molecular dynamics simulations, we model the bonding of hydrocarbon systems by the reactive many-body bond order potential ($REBO$) due to Brenner [11]. Additionally, we employ a modified Lennard-Jones potential term to describe the van der Waals interactions [12]. Note that for these potentials all interatomic terms are of short range. Thus, we are able use the well-known linked cell technique. We furthermore employ a domain decomposition approach to obtain a parallel implementation. Altogether this results in an approach which possesses a computational complexity of the order $\mathcal{O}(N/P)$, see [13, 8, 10] for details. Here, $N$ denotes the number of particles and $P$ the number of processors. We employ a so-called Parrinello-Rahman-Nosé Lagrangian [14, 15] for the equilibration of the considered systems. In order to deal with the difficulty of velocity-dependent forces in the related equations of motion, we use the numerical time integration scheme of Refson [16] which relies on Beeman's approach [17]. To apply tensile load to the system we employ an external stress-tensor within the equations of the Parrinello-Rahman-Nosé approach [10]. In particular, we linearly increase the longitudinal external stress component over time and compute a discrete stress-strain curve. Under the assumptions that *Hooke's law* [18] is fulfilled and the stress increase is slow enough to be considered adiabatic, we then can calculate an approximative value of the Young modulus by least squares linear regression.

## 3   Numerical Experiments

All simulation runs were performed with our distributed memory parallel molecular dynamics software package TREMOLO [19] on the PC cluster Parnass2 [20]. Furthermore, all simulations were carried out with a time step size of $0.1\,\mathrm{fs}$ at a temperature of $300\,\mathrm{K}$ under normal pressure conditions of $1.01325 \cdot 10^{-4}\,\mathrm{GPa}$. After $50\,\mathrm{ps}$ of equilibration, we applied tensile load with a stress rate of $0.01\,\mathrm{GPa/ps}$ to the different systems under consideration. Throughout our experiments we used periodic boundary conditions. This way, we studied the following systems:

(1) A polyethylene matrix which consists of 10 chains of 1000 $CH_2$ units each; see Figure 1(a). Here, the equilibrated matrix exhibits a density of about $1\,\mathrm{g/cm^3}$.

(2) A capped (10,10) carbon nanotube which is embedded in the polyethylene

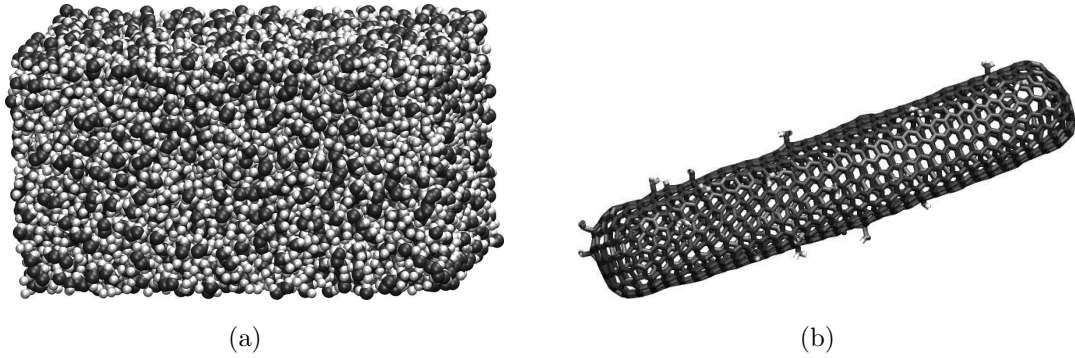(a)                                                          (b)

Figure 1: (a) Equilibrated periodic unit cell of the polyethylene matrix. (b) View of the functionalized carbon nanotube, where $1\%$ of the carbon atoms have been randomly linked to a $CH_2$ unit.

matrix (1). Here we employed only non-bonded interactions between the atoms of the nanotube and that of the matrix.

(3) A capped (10,10) carbon nanotube which is embedded in the polyethylene matrix (1). Now, in addition to the non-bonded interactions of system (2), $1\%$ of the carbon atoms of the nanotube have cross-links to the matrix; see also Figure 1(b).

(4) A capped (10,10) carbon nanotube which is embedded in the polyethylene matrix (1). Now, $5\%$ of the carbon atoms of the nanotube have cross-links to the matrix; see Figure 2.

(5) A capped (10,10) carbon nanotube which is embedded in the polyethylene matrix (1). Now, $10\%$ of the carbon atoms of the nanotube have cross-links to the matrix.

(6) A capped (10,10) carbon nanotube which is embedded in the polyethylene matrix (1). Now, $15\%$ of the carbon atoms of the nanotube have cross-links to the matrix.

(7) A capped (10,10) carbon nanotube which is embedded in the polyethylene matrix (1). Now, $25\%$ of the carbon atoms of the nanotube have cross-links to the matrix.

The nanotube of the systems (2)–(7) is composed of 1136 carbon atoms and is about $67.5\,\text{Å}$ long. To create the embedded systems in the beginning, an artificial potential was employed analogous to the approach described in [21]. The cross-links between the nanotube and the matrix were selected randomly.
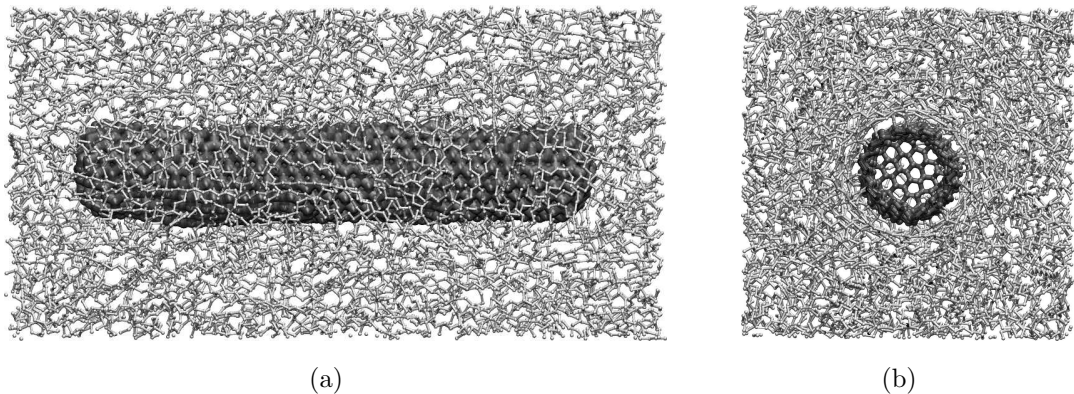
Figure 2: Side view (a) and front view (b) of the periodic unit cell of system (4). Note that we omitted the hydrogen atoms to allow for better visualization. Also, we cut off the front part of the simulation domain in (b).

Table 1: The computed Young moduli $E$ of the systems (1)–(7).

| System | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|
| $E$ [GPa] | 2.88 | 5.97 | 6.21 | 6.78 | 7.01 | 7.13 | 7.29 |

## 4   Results and Discussion

Our results for the Young moduli of systems (1)–(7) are given in Table 1. If we compare the modulus of the polyethylene matrix (1) and that of the composite system with weak nonbonded interactions (2), we see a substantial reinforcement; for a further detailed discussion see [10]. For the systems (3)–(7) we see the following effect of the additional cross-links on the Young modulus: In general, our results show further reinforcement in comparison to the composite system (2). To be precise, we obtain a modulus that is 1.04 times higher for system (3), a modulus that is 1.14 times higher for system (4), a modulus that is 1.17 times higher for system (5), a modulus that is 1.19 times higher for system (6) and a modulus that is 1.22 times higher for system (7) than the modulus of system (2). Note that the rate of reinforcement in comparison to the composite system (2) is growing sublinearly with the amount of cross-links. Figure 3 shows the growth and saturation with higher amounts of cross-links. Our results suggest a logarithmic dependency of the Young modulus of the composite on the rate of cross-links $r$. This way, the Young modulus can be estimated by

$$P(r) = E_0 + \alpha \ln(r). \qquad (1)$$

Here, we determined a value of approximately 0.34 for the factor $\alpha$ and a value of 6.22 GPa for $E_0$ by a parameter fit. The estimator $P$ predicts the Young modulus quite accurate in the range of a cross-link rate of 5 % to 15 %. The over- and underestimation in the lower range is probably due to the random distribution of
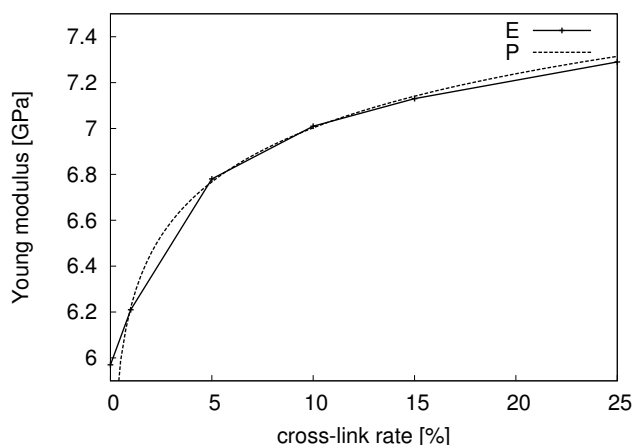
Figure 3: Graph of the calculated Young moduli $E$ of the composite systems (2)–(7) and the estimator function $P$ given in (1).

only a minor number of cross-links. In the range higher than 15 %, the overestimation results from the fact that the Young modulus of the functionalized composite is bounded due to the saturation of the number of cross-links, whereas our simple prediction function $P$ stays unbounded. To verify a more precise functional dependence, more simulation data is necessary.

## 5 Concluding Remarks

Our results show that chemical cross-links increase the Young modulus of a polyethylene nanotube composite. This suggests the possibility to use functionalized nanotubes to reinforce other kinds of polymer-based materials as well.

## 6 Acknowledgments

## References

[1] S. Iijima. Helical microtubules of graphitic carbon. *Nature*, 354:56–58, 1991.

[2] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson. Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature*, 381:678–680, 1996.

[3] B. I. Yakobson and R. E. Smalley. Fullerene nanotubes: $C_{1,000,000}$ and beyond. *American Scientist*, 85(4):324–337, 1997.

[4] S. J. V. Frankland, A. Caglar, D. W. Brenner, and M. Griebel. Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube-polymer interfaces. *J. Phys. Chem. B*, 106:3046–3048, 2002.

[5] G. M. Odegard, S. V. J. Frankland, and T. S. Gates. The effect of chemical functionalization on mechanical properties of nanotube/polymer composites. Technical Report AIAA 2003-1701, American Institute of Aeronautics and Astronautics, 2003.

[6] P. M. Ajayan, L. S. Schadler, S. C. Giannaris, and A. Rubio. Single-walled carbon nanotube-polymer composites: Strength and weakness. *Adv. Materials*, 12:750–753, 2000.

[7] C. Velasco-Santos, A. L. Martínez-Hernández, F. T. Fisher, R. Ruoff, and V. M. Castaño. Improvement of thermal and mechanical properties of carbon nanotube composites through chemical functionalization. *Chem. Mater.*, 15:4470–4475, 2003.

[8] M. Griebel, S. Knapek, G. Zumbusch, and A. Caglar. *Numerische Simulation in der Moleküldynamik. Numerik, Algorithmen, Parallelisierung, Anwendungen.* Springer, Berlin, Heidelberg, 2003.

[9] S. J. V. Frankland, V. M. Harik, G. M. Odegard, D. W. Brenner, and T. S. Gates. The stress-strain behavior of polymer-nanotube composites from molecular dynamics simulations. *Composites Science and Technology*, 63(11):1655–1661, 2003.

[10] M. Griebel and J. Hamaekers. Molecular dynamics simulations of the elastic moduli of polymer-carbon nanotube composites. *Computer Methods in Applied Mechanics and Engineering*, 193(17–20):1773–1788, 2004.

[11] D. W. Brenner. Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. *Phys. Rev. B*, 42(15):9458–9471, 1990.

[12] Z. Mao, A. Garg, and S. B. Sinnott. Molecular dynamics simulations of the filling and decorating of carbon nanotubules. *Nanotechnology*, 10:273–277, 1999.

[13] A. Caglar and M. Griebel. On the numerical simulation of fullerene nanotubes: $C_{100.000.000}$ and beyond! In R. Esser, P. Grassberger, J. Grotendorst, and M. Lewerenz, editors, *Molecular Dynamics on Parallel Computers, NIC, Jülich 8-10 February 1999*. World Scientific, 2000.

[14] M. Parrinello and R. Rahman. Crystal structure and pair potentials: A molecular-dynamics study. *Phys. Rev. Lett.*, 45(14):1196–1199, 1980.

[15] S. Nosé and M. L. Klein. Constant pressure molecular dynamics for molecular systems. *Molec. Phys.*, 50(5):1055–1076, 1983.

[16] K. Refson. Molecular dynamics simulation of solid n-butane. *Physica B*, 131:256–266, 1985.

[17] D. Beeman. Some multistep methods for use in molecular dynamics calculations. *J. Comp. Phys.*, 20:130–139, 1976.

[18] D. S. Chandrasekharaiah and L. Debnath. *Continuum Mechanics*, chapter 9.2. Academic Press, San Diego, 1994.

[19] `http://wissrech.ins.uni-bonn.de/research/projects/tremolo/`. TREMOLO is a dynamically load-balanced distributed memory parallel molecular dynamics simulations software package developed at the *Institut für Numerische Simulation* at the University of Bonn.

[20] `http://wissrech.ins.uni-bonn.de/research/projects/parnass2/`. Parnass2 consists of 128 Intel Pentium II 400 MHz processors connected by a 1.28 GBit/s switched Myrinet.

[21] D. Brown, P. Mélé, S. Marceau, and N. D. Albérola. A molecular dynamics study of a model nanoparticle embedded in a polymer matrix. *Macromolecules*, 36:1395–1406, 2003.