Molecular Modelling for Calculation of Mechanical Properties of SWCNTs/Epoxy Composites: Effect of SWCNTs Diameter

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The present paper studies the effect of the diameter of single walled carbon nanotubes (SWCNTs) on mechanical properties of SWCNTs reinforced epoxy resin composites. Bulk atomistic models of epoxy resin-SWCNTs with different compositions were built and were subject of an extensive multistage equilibration procedure. Molecular dynamics simulations were used to estimate glass transition temperature (Tg) and Young's modulus of epoxy resin and epoxy resin/SWCNTs composites. The Young's moduli generally increased with increasing of SWCNTs content and values range from 1.83 GPa in the case of pure epoxy resins to 3.21 GPa for epoxy resin/SWCNTs (8,8) composite system. Overall, the agreement between predicted values of the material properties and experimental data in the literature is satisfactory.

Keywords: atomistic molecular modeling; mechanical properties; SWCNTs- epoxy resin composites, glass transition temperature

One of the most important and exciting areas of composites research is the development of modelling techniques to predict the response of composite materials. Predictive modelling provides the opportunity to understand better how composites behave in different conditions, to develop materials with enhanced performance for particular industrial applications, and to limit the efforts of synthetic chemists in following the inefficient Edisonian prescription of creating all possible mixtures in order to isolate the desired materials [1-2]. Atomistic molecular modeling techniques are new and powerful methods for polymeric materials investigation at molecular level and have proved to be able to supply macroscopic characteristics such as mechanical properties [3].

The atomistic modelling of polymers for calculating mechanical properties has been researched for several years. A static method was developed early by using molecular mechanics (MM) techniques [4]. Stress–strain simulations in molecular dynamics (MD) have been employed for some time [5]. A more accurate method to assess the mechanical properties is density functional theory (DFT) *ab initio* approach which considers more details about the electrons and the ions but is slow, computationally expensive and not applicable for large systems as those investigated in the present paper which consist of polymeric chains and carbon nanotubes with a total number of atoms of about 5000 [6].

Mechanical properties are of relevance for all applications of polymers in industry, medicine, household, and others. The improvement of mechanical properties in general and the better fitting of specific properties to defined applications is a continuous goal of polymer research. Several research groups reported the role of carbon nanotubes (CNTs) in the reinforcement of polymer matrices. The extent of mechanical reinforcement depends on several factors, including uniformity of dispersion, degree of alignment and the strength of polymer–CNTs interfacial bonding which are difficult to control and measure experimentally. To provide such crucial insights computationally molecular modelling might be successfully used. Recent studies indicate that both the alignment and dispersion qualities are dependent on the carbon nanotubes species in terms of diameter [7]. E.g., poly(m-phenylenevinylene) exhibits a selective affinity towards the CNTs of diameters ranging between 1.35 and 1.55 nm [8].

Composites based on epoxy resins and CNTs are promising for the development of new classes of multi-functional advanced materials. Embedding of carbon nanotubes in epoxy resins matrices offers an attractive route to reinforce polymer and to provide electronic properties based on morphological modification or electronic interaction between the two components [9]. However, there are very few works reporting the computational characterization of epoxy resins-SWCNTs composites since performing these simulations is not a trivial task. It can be difficult to obtain mechanical properties from atomistic simulation that compare well with experimentally measured values due to the difficulty of building the models and the various parameters involved [3, 10].

In the present work, SWCNTs with a variety of diameters are combined with epoxy resin and the composites are subjected to virtual uniaxial traction tensions. The mechanical properties of composites containing SWCNTs with different diameters are compared and therefore the effects of SWCNTs diameter on Young's modulus of SWCNTs/epoxy resin composites are investigated. Furthermore, molecular dynamics simulations were employed to assess the glass transition temperature (*Tg*) of epoxy resin.

Molecular modelling simulations

Construction of the computational bulk models

The molecular models construction and subsequent simulations were conducted using the Materials Studio 5.0 molecular modeling package of Accelrys and the COMPASS forcefield [9]. The non-bond interactions with a cutoff distance of 9.5Å including van der Waals and electronic static forces were considerated.

A single repeat unit of epoxy resin, i.e. diglycidyl ether of bisphenol A, has been manually constructed and minimized in order to obtain a stable starting structure. Conversely, the SWCNTs with different diameters, (2,2), (4,4), (6,6), (8,8) are available as standard model in software data base. Charge groups have been assigned to

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Name of model	Composition of the model (w/w)	No. of atoms in the model	Av. lateral dimension of the model (Å)
Epoxy resin	100	4590	39.73
Epoxy resin/SWCNTs (2,2)	98/2	4654	38.48
Epoxy resin/SWCNTs (4,4)	98/2	4718	38.30
Epoxy resin/SWCNTs (6,6)	98/2	4686	37.82
Epoxy resin/SWCNTs (8,8)	98/2	4846	39.15

Table 1
MAIN CHARACTERISTICS OF THE COMPUTATIONAL MODELS

fragments of each repeated unit and SWCNTs. The isolated epoxy chain configurations were then generated starting from the repeating units using Build Polymer tool of the software.

Computational bulk models of epoxy resin/SWCNTs (2,2), epoxy resin/SWCNTs (4,4), epoxy resin/SWCNTs (6,6) and epoxy resin/SWCNTs (8,8) were implemented, with 98:2 weight ratio under periodic boundary conditions employing the Amorphous cell module. This allows us to determine the influence of SWCNTs diameter on the mechanical behaviour of the composite systems. Each of the cubic bulk models consists of about 5000 atoms and the dimension was about 40Å. The main features of computational bulk models are depicted in table 1. Since the systems contain aromatic elements the chain packing stage was performed for all the models at a very low initial packing density (0.1 g/cm^3) [2].

Equilibration of the computational bulk models

All initial packing models were subject to an extensive multistage equilibration procedure. The main reason is that initial packing models contain considerable interatomic overlaps [10], thus very large forces acting in individual atoms may occur at the beginning of the equilibration, which lead to atomic velocities far beyond the respective average values in an equilibration situation.

There is also the additional problem that the packing models need to be slowly compressed from a density of about 0.1 g/cm^3 to the respective real density via NPT-MD runs. A first equilibration cycle consisted in five steps of energy minimisation and MD simulations in which conformation and non-bonded pair interaction terms in the force field have been appropriately scaled down, by scaling factors from 0.01 to 1, as depicted in table 2 [2, 10].

Each step of minimisation was performed using two different algorithms, initially Steepest descent algorithm was used since it is an extremely robust method most likely to generate a lower-energy structure, generally applied for the first 10-1000 steps of minimisation. Afterwards, the most advanced Conjugate gradient-Fletcher-Reeves algorithm (that can be unstable if the conformation is far away from a local minimum) was used to achieve efficient convergence to the minimum. The final convergence criterion was to meet at derivative of less than 0.001 kcal·mol^{-1}.

Each step of MD-NVT (constant number of molecules volume and temperature (300K)) simulations runs for 300.000 steps and the time step was 1 fs. The Berendsen thermostat was used to control the temperature during MD simulations. After this equilibration cycle each packing model was subject of a short MD-NPT (constant number of molecules, pressure and temperature) simulation at p = 1 GPa and T = 300 K for about 5000 steps. MD-NPT simulations were performed in order to compress the model and to reach the density of the real material. The Berendsen barostat was used to control the pressure during NPT-MD simulations. After the compression stage the systems show a certain degree of unrealistic tension indicating that the simulated packing models need further equilibration. This was performed *via* repeating the equilibration cycle consisting of five steps of MM and MD calculations each one characterised by scaling factors. The overall simulation time requested for the equilibration procedure for each of the models was about 5 ns.

Table 2
FORCEFIELD SCALING FACTORS FOR COMPUTATIONAL MODELS REFINEMENT PROCEDURE

Scaling Factor	Bond	Non-bond
Step 1	0.01	0.01
Step 2	0.1	0.01
Step 3	0.1	0.1
Step 4	1	0.1
Step 5	1	1

Investigation of the computational bulk models

In order to test the mechanical properties the Elastic Properties Analysis tool implemented in the software was used. Elastic Properties Analysis tool is using a static approach originating in 1986 [5]. The input data required by this method consists in sets of coordinates of well equilibrated configuration. For each configuration submitted for static elastic constants analysis, a total of 13 minimisations were performed. The first consists of a Conjugate gradients minimisation of the undeformed amorphous system. The target minimum derivative for this initial step is 0.1 kcal/Å. In order to reduce the time required by this calculation, well equilibrated models were submitted for the analysis. Following this initial stage, three tensile and three pure shear deformations were applied to the minimized undeformed computational bulk models and the systems were reminimised following each deformation. The internal stress tensor is then obtained from the analytically-calculated virial equation, equation (1), and used to estimate the six columns of the elastic stiffness coefficients matrix.

$$\sigma = -\frac{1}{V_0}\left[\left(\sum_{i=1}^{N} m_i (v_i v_i^T)\right) + \left(\sum_{i<j} r_{ij} f_{ij}^T\right)\right] \qquad (1)$$

where i is the particle number, m_i, v_i and f_i are the mass, velocity of the particle and force acting on the particle, respectively, and V_0 is the volume of the system. Finally, by reversing the elastic stiffness matrix the compliance matrix was obtained and from that the elastic moduli referred to the three perpendicular directions of the systems were calculated.

In order to assess the glass transition temperature MD simulations were conducted started from 450 K under a pressure of 0.1 MPa using NPT ensembles. Temperature was decreased with a rate of 10°C/200 ps and was controlled with Berendsen thermostat. Each subsequent simulation was started from the final configuration obtained at the previous temperature. The MD simulations were performed with a step of 1 fs.

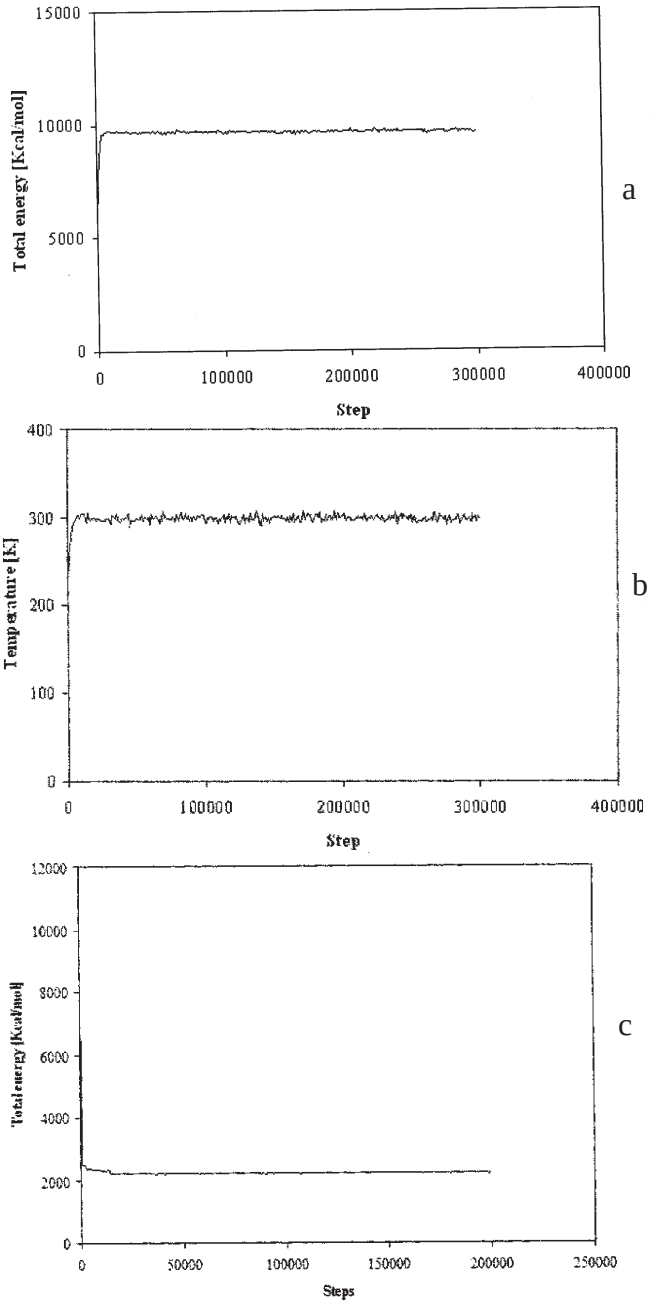

Fig. 1. Temperature and total energy profile *vs*. step (a) and (b) during the molecular dynamics calculations and total energy *vs*. step (c) during the minimisation, of epoxy resin/SWCNTs (6,6) bulk model during the 5th step of equilibration procedure

Results and discussions

The goodness of each model has been analysed, all the systems achieve convergence (convergence criterion for molecular mechanics calculations was to meet a total energy derivative of less than 0.001 kcal·mol^{-1}) and reach stable values for total energy and temperature after each step of the MD simulations.

Figure 1 illustrates the fluctuation of the total energy (a) and temperature (b) during the molecular dynamics calculations and variation of the total energy during the molecular mechanics calculations (c), for the system epoxy resin/SWCNTs (6.6) during the 5th step of equilibration procedure. It can be observed from Figure 1 that the system achieves convergence to the minimum during the minimisation steps (fig. 1c), conversely the temperature and total energy presets constant values during the molecular dynamics calculations (fig. 1a, 1b). Therefore, it was concluded that the packing models should be sufficiently equilibrated and confirms the reliability of the protocol for generating realistic packing models.

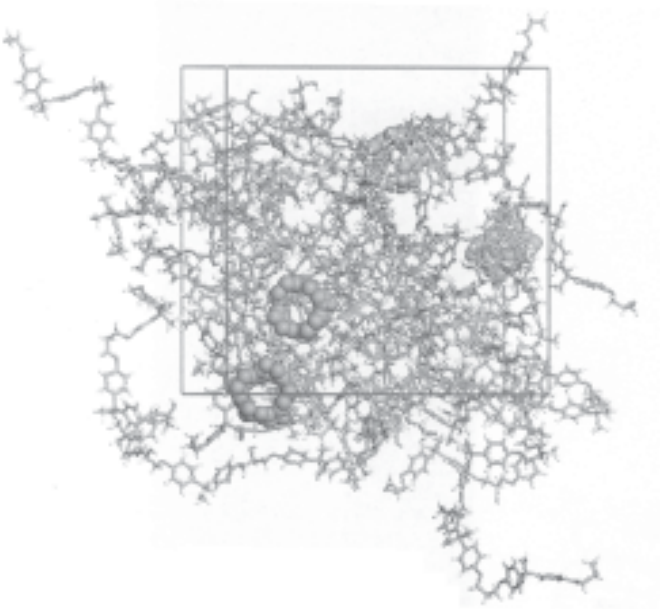

Fig. 2. Computational bulk model of epoxy resin/SWCNTs (8.8) after the equilibration procedure, random and uniform distribution of polymeric chains and SWCNTs (8.8) within the bulk model

Concerning the composite systems morphology, as it can be seen from figure 2, SWCNTs (8.8) exhibit a high dispersibility within the epoxy matrix. A homogeneous and random dispersion of both SWCNTs and polymeric chains was achieved after equilibration procedure with only very few agglomerates remaining in the case of the composites epoxy resin/ SWCNTs (2.2) and epoxy resin /SWCNTs (4.4).

After the validation of the computational models the activity was focused on the assessment of mechanical behaviour. The method used here for calculating the elastic constants is one for static deformation of periodic atomistic models. The 6×6 elastic constant matrix is determined by partial derivatives of the stress tensor with respect to the deformation. The procedure for Young's moduli calculation was the same described elsewhere [12].

The predicted Young's moduli from the MD simulations at 300 K range from 1.83 GPa in the case of pure epoxy resin, to 2.74 GPa in the case of SWCNTs (6,6)/epoxy resin and to 3.21 GPa in the case of SWCNTs (8,8)/epoxy resin composite system as depicted in table 3. An increase of up to 170% of the elastic moduli was observed upon the addition of SWCNTs (8,8). Generally a reinforcement of the epoxy resin was observed with the addition of the SWCNTs. However, the reinforcement was related to the SWCNTs diameter, the maximal value of Young's modulus (3.21 GPa) was obtained for the composite system SWCNTs (8,8)/epoxy resin thus we can conclude that the best reinforcement of epoxy resin is provided by SWCNTs (8,8).

The differences in the reinforcing efficiency between SWCNTs (2,2), SWCNTs (4,4), SWCNTs (6,6) and SWCNTs (8,8) is most likely due to different interaction energies between the carbon nanotubes and epoxy resin and to SWCNTs dispersion uniformity. Some preliminary investigations indicate that the interaction energy between epoxy resin and SWCNTs (8,8) is stronger than that of the epoxy resin and SWCNTs (2,2) or epoxy resin and SWCNTs (4,4). Moreover, the solubility coefficient of SWCNTs (determine the miscibility of carbon nanotube) is related to the carbon nanotubes diameter [8]. The predicted solubility coefficient for SWCNTs (4,4) is $\delta=28$ $(J/cm^3)^{-0.5}$, for SWCNTs (6,6) $\delta=25$ $(J/cm^3)^{-0.5}$ and for SWCNTs (8,8) $\delta=22$ $(J/cm^3)^{-0.5}$ [8]. Assuming Flory-Huggins theory [14-

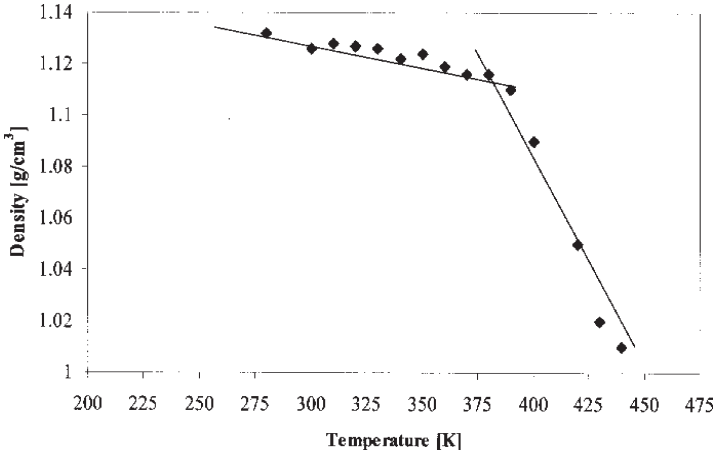

Fig.3. Variation of the density of the epoxy resin system as a function of temperature

Material	Young's Modulus [GPa]	Standard deviation
Epoxy resin	1.83	0.22
Epoxy resin-SWCNTs (2,2)	2.15	0.27
Epoxy resin-SWCNTs (4,4)	3.02	0.39
Epoxy resin-SWCNTs (6,6)	2.74	0.24
Epoxy resin-SWCNTs (8,8)	3.21	0.29

Table 3
SUMMARY OF ELASTIC MODULI FOR EPOXY RESIN-SWCNTS COMPOSITE SYSTEM

15] which predicts that components with similar δ values lead to low repulsion and considering the solubility coefficient of the epoxy resin (δ=18.80 $(J/cm^3)^{-0.5}$), the SWCNTs (8.8) should form a homogeneous material with the epoxy matrix.

Similar observations, which demonstrate that the reinforcing efficiency depends on the SWCNTs diameter were found in [16]. Concerning numerical values of Young's modulus, they turned out to be slightly lower when compare with other studies about the mechanical properties of epoxy resins, which range from 2.83 to 3.5 GPa [12, 16], and of epoxy resin/CNTs composites which range from 3.5 to 4.6 GPa [16] .

The lower stiffness displayed by the computational systems might be due to the fact that in our models just few covalent interactions between cross-linking agent and epoxy resin chains were taking into account which means that the simulated systems show a low degree of cross-linking in comparison with the real material. In the absence of covalent chemical bonding, the interfacial bond strength comes mainly from the electrostatic and van der Waals forces which are weaker when compared with covalent bonding and might lead to a slightly lower reinforcement. From MD calculations the density of the epoxy resin system at each temperature was calculated from the average specific volume of the system as shown in figure 3. A discreet increase of the density with decreasing temperature was observed for temperature values ranging from 260 to 380 K. A clear change in the slope of the density curve was observed for the temperature ranging from 380 to 480 K. The change in the slope of the density curve defines the values of the glass transition temperature, at 380 K, where epoxy resin passes from a glassy state to rubbery state [12]. The *Tg* predicted from MD simulations is in good agreement with experimental data from the literature [13]. This indicates the properness of both the protocol and the forcefield used here to calculate the *Tg*.

Conclusions

MD simulations were used for calculating the elastic constants and *Tg* of pure epoxy resin and epoxy resins-SWCNTs composite systems.

Generally a reinforcement of the epoxy resins was observed with the addition of the SWCNTs. Among the composite systems studied in this article the epoxy resin-SWCNTs (8,8) composite exhibited the highest enhancement of the Young's modulus, and it was followed by composites epoxy resin-SWCNTs (6,6) and epoxy resin-SWCNTs (2,2) thus the reinforcement was related to the SWCNTs diameter.

Concerning numerical values of *Tg*, they turned out to be consistent with other studies from the literature.

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