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Comparison of COMPASS and PCFF in Calculating Mechanical Behaviors of Aramid Fiber by Means of Molecular Dynamics

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Abstract

In order to compare COMPASS and PCFF in calculating the micro mechanical behaviors of aramid fiber, the molecular dynamic method was employed to establish the COMPASS-based and PCFF-based PMLA models in Materials Studio (MS) software. There were 10 models in each force field, all of which underwent structural optimization and relaxation processing. After every model reached the state of energy minimization, the molecular dynamics simulation was carried out. The simulation results demonstrate that compared to PCFF, COMPASS is less erroneous, more reliable and with more uniform results in calculating the mechanical behaviors of aramid fiber by means of molecular dynamics.

Key words

COMPASS, PCFF, Aramid fiber, Molecular dynamics, Mechanical properties.

1. Introduction

As the computer simulation theories mature and the modern computer technology develops rapidly, the computer simulation technology has made further progress [1, 2]. Highly dependent on computer, molecular simulation is also called "computer experiment" or "computer simulation". With the parameterization of force field, this technology becomes more mature [3]. Molecular simulation is the modelling of physical or chemical processes to explain experimental phenomena and test experimental feasibility [4]. Molecular simulation methods can be divided into quantum mechanics and statistical mechanics, and the latter one includes molecular mechanics (MM), molecular dynamics (MD) and Monte Carlo (MC) [5]. With MD, the equilibrium state and dynamic properties of models can be obtained, and some high energy barriers can be crossed to search larger conformation space for the lowest energy conformation. Therefore, we select MD as our simulation approach.

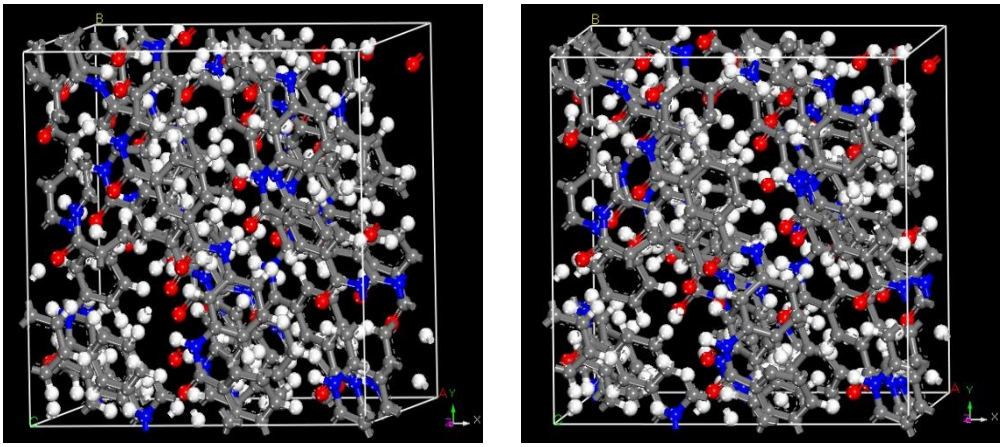
Due to its special paper structure and excellent mechanical, electrical and chemical properties, meta-aramid insulation paper is widely applied in the fields of communications, electric engineering, military project, etc. [6] Researches on aramid insulation paper gradually mount up [7, 8]. Literatures [9, 10] are such studies based on molecular simulation. As force field is the basis of molecular dynamic simulation, force field selection determines how accurate the simulation result will be [11, 12]. COMPASS and PCFF are two commonly-used force fields in molecular dynamic simulation. Yet there is no clear-cut reports on which one is better for the molecular dynamic simulation of aramid fiber models.

In this paper, the MS software is used to compare COMPASS and PCFF by means of molecular dynamics. There are 10 models in each force field, all of which undergo structural optimization and relaxation processing. After every model reaches the state of energy minimization, the molecular dynamics simulation is carried out. We think that shorter mechanical wavelength corresponds to smaller deviation between the measured value and the mean value as well as more uniform and reliable simulation result. The force field that obtains shorter mechanical wavelength is the desired force field.

2. Model Construction

Firstly, the Visualizer module in the MS software is employed to simulate the meta-aramid fiber amorphous model whose degree of polymerization (DP) is 10. Then, we build up 20 such models in the Amorphous Cell module, half in COMPASS and half in PCFF. These models undergo energy optimization and relaxation processing in the Discover module, after which all of them are in the steady state. Then, we carry out molecular dynamic simulation on them, calculating

the mechanical parameters in the two force fields. The number of chains of aramid fibers is 2 and the target density of the model is set as 1.2 g/cm^3.



(a) PCFF force field (b) COMPASS force field

Fig.1. The MPIA Fiber Dynamics Model

3. Simulation Methods and Parameter Settings

After the models are established, the model energy is so high that we need to relax them. For relaxation process, the temperature is increased from 300K to 600K first, and then returns to 300K. The relaxation process is repeated every 100K at the medium convergence level by means of smart minimizer optimization, with the maximum iteration time of 5,000. The molecular dynamic simulation will be conducted after the relaxation process is completely finished.

The simulation is undertaken in the Discover module. With the NVT ensemble, the relaxed model is simulated at the time of 200ps and the temperature of 363K; then, the NPT ensemble is used for simulation at the same time length under the standard atmospheric pressure. The initial molecular velocities are sampled in accordance with Maxwell distribution, and the solution of Newton equation is found by using leapfrog/velocity Verlet method. The dynamic data is collected every 5,000 steps for data analysis. Under the two ensembles, the simulated time step is 1fs, the cut-off radius is 9.5Å, and the spline width is 1Å.

In the simulation process, the Andersen thermostat [13] and Barendsen barostat [14] are used to maintain constant temperature and pressure, while the Atom Based approach is used to calculate Van der Waals forces. For other parameters, please refer to the literature [10].

4. Results and Discussion

4.1 Evaluating Energy Optimization

The fluctuating range of model energy and temperature is one criteria to decide whether the model energy is optimized in molecular dynamic simulation. Generally, if the temperature and model energy fluctuate within the range of 5%-10%, the model energy can be regarded as reaching the optimal state [15]. Model energy mainly includes potential and non-bond energy, and the final temperature is 300K. According to Figure 2, the temperature fluctuates little around 300K; the energy fluctuates greatly the time before 100,000ps and then levels off. If judged by the equilibrium of complex wave system, the meta-aramid fiber amorphous model has reached the equilibrium state, meaning that the simulation result is reliable.

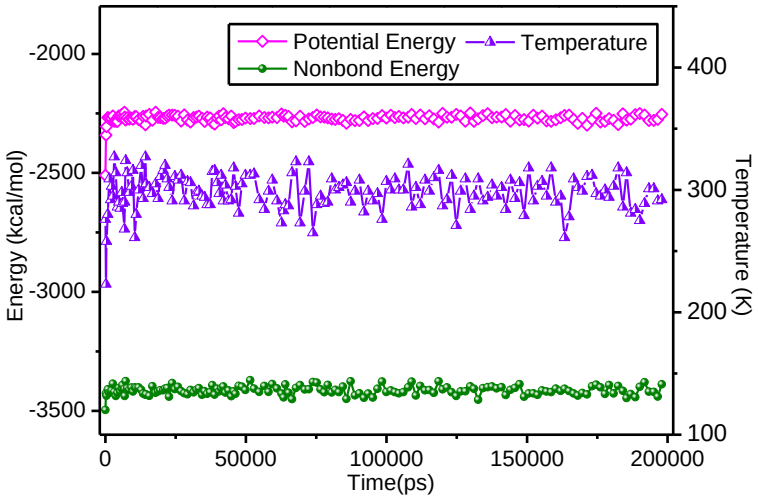


Fig.2. Energy and Temperature Fluctuation Curves

4.2 Mechanical Parameters

From the elastic mechanics we can see that the most general relationship between the stress and strain of the solid materials can be expressed by the generalized Hooke's law:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \\ \gamma_{yz} \\ \gamma_{zx} \\ \gamma_{xy} \end{bmatrix} \tag{1}$$

where C_{ij} is a 6×6 elastic coefficient matrix element, at a total number of 36 according to formula (1). All the mechanical parameters of the material can be derived from its elastic coefficient matrix, where σ is stress, ε is strain, τ is shear stress, and γ is shear strain. For the anisotropic material, there is only 21 independent elastic coefficients due to the presence of elastic strain energy which lets $C_{ij}=C_{ji}$; for isotropic body, there are only two independent elastic coefficients C_{11} and C_{12}. The mechanical parameters of the material can be calculated based on elastic mechanics: bulk modulus *(K)*, shear modulus *(G)*, Poisson's ratio *(ν)*, tensile modulus *(E)*, *K/G* value (the ratio of bulk modulus to shear modulus) of the material can be calculated according to the elastic mechanics. Modulus and shear modulus ratio), Cauchy pressure (C_{12}-C_{44}) (denoted herein with *C*), etc. These parameters can be used to represent various mechanical properties of materials [16]. The inverse matrix of the elastic coefficient matrix is found, with S_{ij} denoting the inverse matrix element. Then, the mechanical parameters are obtained according to the Reuss value [17, 18].

$$a = \frac{1}{3}\left(S_{11} + S_{22} + S_{33}\right) \tag{2}$$

$$b = \frac{1}{3}\left(S_{12} + S_{23} + S_{31}\right) \tag{3}$$

$$c = \frac{1}{3}\left(S_{44} + S_{55} + S_{66}\right) \tag{4}$$

And we have:

$$K = \left[3(a + 2b)\right]^{-1} \tag{5}$$

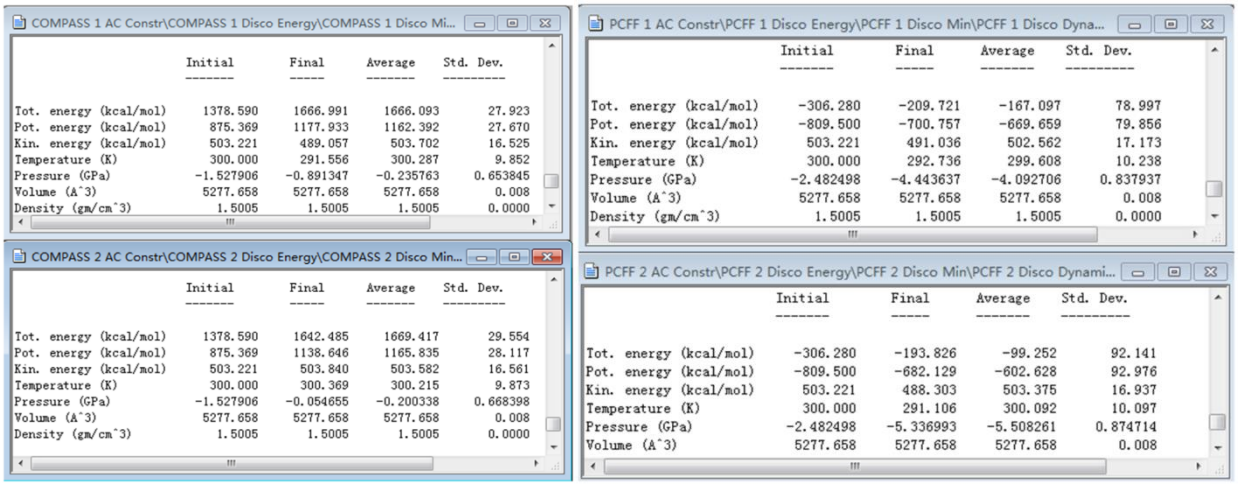
$$G = \frac{5}{4a - 4b + 3c} \tag{6}$$

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \tag{7}$$

4.3 Simulation Results Analysis

Models that are established in the same force field have different initial energies. Figure 3 shows the data of model energy in COMPASS and PCFF, respectively. The parameter value will vary in different force fields by means of molecular dynamic simulation, which means that the simulation result will have a deviation. We think that the deviation is caused by force field parameters. If the deviation is small in a force field, it means that the random error is small, and

the simulation result is highly reliable. In this case, it requires less times of verification and shorter simulation time.



COMPASS 1 AC Constr\COMPASS 1 Disco Energy\COMPASS 1 Disco Mi...

	Initial	Final	Average	Std. Dev.
Tot. energy (kcal/mol)	1378.590	1666.991	1666.093	27.923
Pot. energy (kcal/mol)	875.369	1177.933	1162.392	27.670
Kin. energy (kcal/mol)	503.221	489.057	503.702	16.525
Temperature (K)	300.000	291.556	300.287	9.852
Pressure (GPa)	-1.527906	-0.891347	-0.235763	0.653845
Volume (A^3)	5277.658	5277.658	5277.658	0.008
Density (gm/cm^3)	1.5005	1.5005	1.5005	0.0000

COMPASS 2 AC Constr\COMPASS 2 Disco Energy\COMPASS 2 Disco Min...

	Initial	Final	Average	Std. Dev.
Tot. energy (kcal/mol)	1378.590	1642.485	1669.417	29.554
Pot. energy (kcal/mol)	875.369	1138.646	1165.835	28.117
Kin. energy (kcal/mol)	503.221	503.840	503.582	16.561
Temperature (K)	300.000	300.369	300.215	9.873
Pressure (GPa)	-1.527906	-0.054655	-0.200338	0.668398
Volume (A^3)	5277.658	5277.658	5277.658	0.008
Density (gm/cm^3)	1.5005	1.5005	1.5005	0.0000

PCFF 1 AC Constr\PCFF 1 Disco Energy\PCFF 1 Disco Min\PCFF 1 Disco Dyna...

	Initial	Final	Average	Std. Dev.
Tot. energy (kcal/mol)	-306.280	-209.721	-167.097	78.997
Pot. energy (kcal/mol)	-809.500	-700.757	-669.659	79.856
Kin. energy (kcal/mol)	503.221	491.036	502.562	17.173
Temperature (K)	300.000	292.736	299.608	10.238
Pressure (GPa)	-2.482498	-4.443637	-4.092706	0.837937
Volume (A^3)	5277.658	5277.658	5277.658	0.008
Density (gm/cm^3)	1.5005	1.5005	1.5005	0.0000

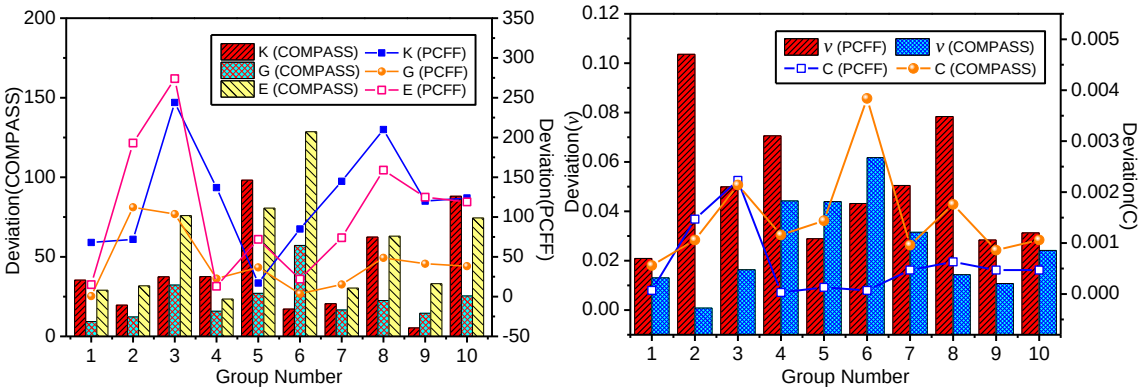
PCFF 2 AC Constr\PCFF 2 Disco Energy\PCFF 2 Disco Min\PCFF 2 Disco Dynami...

	Initial	Final	Average	Std. Dev.
Tot. energy (kcal/mol)	-306.280	-193.826	-99.252	92.141
Pot. energy (kcal/mol)	-809.500	-682.129	-602.628	92.976
Kin. energy (kcal/mol)	503.221	488.303	503.375	16.937
Temperature (K)	300.000	291.106	300.092	10.097
Pressure (GPa)	-2.482498	-5.336993	-5.508261	0.874714
Volume (A^3)	5277.658	5277.658	5277.658	0.008

(a) (b)

Fig.3. The energy Data of all Models by Using Dynamic Simulation at the Temperature of 298K in COMPASS (a) and PCFF (b), Respectively

Through the analysis of the mechanical results of all models, we obtain the deviation value of mechanical parameters (as shown in Figure 4).



(a) (b)

Fig.4. The Deviation of Mechanical Parameters in Different Force Fields

It can be seen from Fig. 4 that the fluctuation amplitude of K, G, E, v deviations calculated in PCFF is larger than those in COMPASS, except for the fluctuation amplitude of C. However, the deviation of C in both force fields is within the range of 0-0.004GPa, which is so small that exerting little influence on the final calculation result. In other words, the C value can be calculated in either force field. In general, compared to PCFF, COMPASS is less erroneous, more reliable and with

more uniform results in calculating the mechanical behaviors of aramid fiber by means of molecular dynamics.

Conclusion

The molecular dynamic method is employed to compare COMPASS and PCFF in calculating the micro mechanical behaviors of aramid fiber. The corresponding dynamic simulation results demonstrate that:

(1) According to the energy optimization criterion, the aramid fiber amorphous model has reached the equilibrium state and the simulation results are reliable.

(2) Models that are established in the same force field have different initial energies. The deviation is caused by force field parameters.

(3) Compared to PCFF, COMPASS is less erroneous, more reliable and with more uniform results in calculating the mechanical behaviors of aramid fiber by means of molecular dynamics.

Acknowledgement

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