Molecular Dynamics Investigation of the Compression and Shearing of Polymer Nano-Composite Systems

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Abstract

Using molecular dynamics soft package LAMMPS, we investiage the procedures of compression and shearing of Polymer Nano-sized-fillers Composits (PNCs) based on well parameterized coarsed-grained model. The addition of the nano-sized fillers to the polymer matrix reinforced the mechanical properies of the system. Interestingly, at above or beneath the glass transition temperature, it behaves independent responses to the coppression or the shearing, and the mechanism behind these phenomena are different. The further analysis of Radius Distribution Function (RDF), and the change of the contacting number between polymer and filler, suggest that the reinforcement of the mechanical properties depends on various factors, such as the size and the shape of the filler, the strength of the interaction between polymer and filler, and etc..

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Introduction

From long ago till recently, people are devoted to the discuttion and investigation of improving the performances of polymer product to meet their different desire. By adding nano- or micro-sized fillers to the polymer matrix, we found thus we are able to change the polymers' mechanical, optical, chemical or electrical properties. (1–6) But the mechanism of the reinforcement of the Polymer Nano-sized-filler Composite (PNC) are still elusive. It is widely acknowledged that there are many influencing factors to this matter, such as, the shape and the size of the filler, the molecular weight of the polymer, the degree of crosslinking of the polymer matrix, the strength of the interaction between the polymer and the filler, the mass-loading of the filler, and dispersity of the filler in the polymer matrix. As the development of the Nano-technology, we already get some advance from both experimental and theoretical points of view, however, the response of NPC to the compression and the shearing, and the mechanism behind are not very well studied and need more profound insigts.

We now are able to use computer simulation to study PNC systems at the atom scale in detail, taking advantage of fast growth of the computer science and technology. Dilip Gersappe depicted a Coarse-Grained (CG) Model of PNC system in 2002, and investiaged the PNC system responses to the tensile (7). Aki Kutvonen and etc. then studied the tensile of the PNC system using a CG model, and demonstrated that the size, the shape, the mass loading and the surface area of the filler will affect the properties of the PNC system. (1, 8) Many other models are then been designed in different scales trying to simulate the tensile, the compression of the PNC systems, and to analyze the inflences of the dispersity of the filler, the strength of the interaction between the polymer and the filler, and other factores, to the properties and the performances of the PNC system. (7, 9–12)

Experimental and theoretical models are developed fast and have been studied widely, however, the compression and the shearing of the PNC system are seldomly investigated and the mechanism is still under consideration. We thus simulate the compression procedure of the PNC system, using a CG model built and manipulatd by the molecular dymamics soft package LAMMPS (13), to investigate the response of PNC to the compression, and describe the mechainism of the reinforcement by the filler to the system. All our analysis of the result are with the help of the software Visual Molecular Dynamics (VMD) (14)

Theory

Methods

We build up a coarse-grained molecular dynamics model to simulate the NPC systems with LAMMPS, get the trajectory of each production run, then analyze the result using VMD.

The Coarse-Grained Model

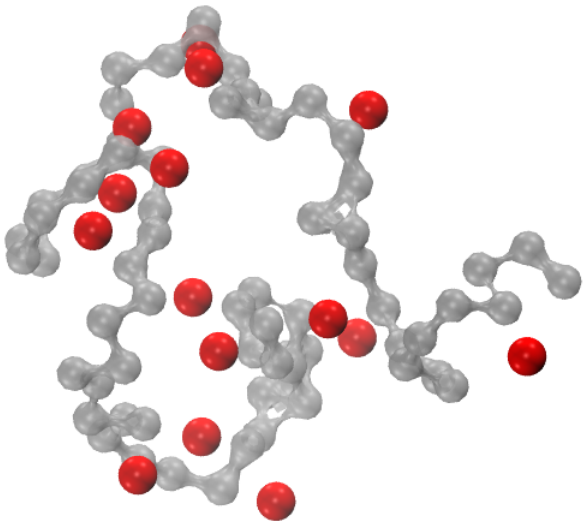

Figure 1: A snapshot of the CG PNC system, taken with VMD. (2)

Using Self-Avoid Walking (SAW) method, we firstly put N polymer chains into a cubic Periodic Boundary Condition (PBC) box. There are L monomers in each chain, and the mass of each monomer is 56 representing a sum of 4 carbon and 8 hydrogen atoms. All bond lengths are set to 4.7 $\mathring{A}$. Then we put M fillers into the system randomly. 1

The force field we use in our model is simply the Lennard-Jones potential (L-J potential) eq. 1, we modify it according to our desire to the L-J potential with radii cut at some certain distance (eq. 2).

$$p^{LJ}(r_{i,j}) = 4\epsilon_{i,j}\left[\left(\frac{\sigma_{i,j}}{r_{i,j}}\right)^{12} - \left(\frac{\sigma_{i,j}}{r_{i,j}}\right)^{6}\right] \tag{1}$$

$$p(r_{i,j}) = \begin{cases} p^{LJ}(r_{i,j}) - p^{LJ}(r_c) & (r_{i,j} < r_c) \\ 0 & (r_{i,j} \geq r_c) \end{cases} \tag{2}$$

$\epsilon_{i,j}$ and $\sigma_{i,j}$ are respectively the strength of the interaction, and the equilibration distance of the interacting atom-pair i, j under consideration.

Protocols of Molecular Dynamics Simulation

After all chains and fillers are positioned in our PBC box, the PNC system is minimized using NVE with a limitation imposed on the distance that atoms are allowed to move in one timestep, in our system, $0.05\mathring{A}/fs^{-1}$. When the energy of the system reaches the minimum, we compress the system and equilibrate it at $1000K$ (which is adjustable), and then lower it stepwise by the decrement of $50K$, to our desired temperture T_{eq} (i.e., $200K$ in our compression simulation, and $600K$ in the shearing one), the whole procedure is performed using NVT updates by far. Equilibrated under T_{eq}, the system is then relaxed using NPT updates to the pressure P_{eq}. The system is ready for any molecular dynamics production run.

The Tensiling

$1.1 \times 10^{-5}\mathring{A}/fs$

The Compression

During the compression procedure, we use the so-called $NL_x\sigma_y\sigma_z T$ ensemble, under which we compress the system along the X-axis, and keep the pressure on other directions unchanged at T_{eq}. The rate of the compression is $1.0 \times 10^{-11}\mathring{A}/fs$.

The Shearing

Setup of the Systems

Here is the list of the potential parameters in each system (the substripts p and f represents polymer and filler respectively, the energy unit is $KCal/mol$ and the length unit is $\mathring{A}$):

Simulation	System	$\epsilon_{p,p}$	$\sigma_{p,p}$	$\epsilon_{p,f}$ [*]	$\sigma_{p,f}$ [†]
S1	Polymer	1.13	4.7	-	-
S2	Polymer-LF	1.13	4.7	4.52	9.2
S3	Polymer-MF	1.13[*]	4.7	4.52	6.1
S4	Polymer-SF	1.13	4.7	4.52	4.6

[*] we keep $\sigma_{f,f} = 0.25\sigma_{p,p}$ for all systems.
[†] Except $r_{cp,f} = 2.1\sigma$, $r_c = 2.1\sigma$ for all i, j atom-pairs

Table 1: List of simulations

Results

Discussion

The Glass Transition Temperature of PNC

The Glass Transition Temperature of the system considered is expected before hand, since we want to have our result comparable with experiments and the real physical phenomenon.

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