THE ENHANCEMENT MECHANISM AND DEFORMATION ANALYSIS OF POLYETHYLENE INCORPORATED WITH POSS BY NANOINDENTATION SIMULATION

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Abstract. In this paper, the nanoindentation tests on the two models of neat polyethylene (PE) and the polyethylene incorporated with 25 wt.% POSS (POSS-PE) are performed to reveal the reinforcing mechanism of the mechanical properties. The molecular mechanics method is adopted to eliminate the temperature effects. After the loading and unloading processes, the hardness and Young’s modulus are calculated through the curve of loading versus displacement. Compared with PE, these mechanical properties of POSS-PE are improved dramatically. To interpret such enhancement effect, first we compare the average displacements of two models. The results show that the average displacement of POSS-PE is much smaller than that of PE, i.e., the deformation of PE is restrained by POSS unit. Utilizing the slipping models, we then analyze the relationship between loading drop phenomenon and slipping energy. From the simulation results, it is believed that the protrudent slipping energy is corresponding to the loading drop exactly, and the slipping between molecular chains is the main source of the loading drop. Furthermore, the average slipping energy of POSS-PE is smaller than that of PE, which implies that the slipping of PE is suppressed by POSS unit.

1. INTRODUCTION

The organic-inorganic nano-hybrid materials are a novel composite materials developed in recent years. With some particular modifiers, conventional organic matter can be modified to prepare new composite materials with special properties. Hybrid materials based on POSS are hot topic of research in the past few years [1-4]. They have wide potential applications in many engineering fields, such as automobile engineering, optical engineering and aeronautical engineering [5,6]. POSS is a class of multifunctional molecules (Fig. 1). It is a cage of silicon and oxygen atoms having the formula \((RSiO_{1.5})_n\), where \(R\) is an inert organic group or active functional group. On the basis of different \(R\) groups, composite materials will generate corresponding characteristics. Among them, the mechanical properties, such as elastic modulus and hardness, are very important. Especially, for thin membrane, hardness is almost an indispensable performance. In order to measure these properties of thin-film materials, nanoindentation method is always used [4,7-11]. For instance, Zeng [4] studied the hardness and size effect of polystyrene incorporated with POSS under square indenter by using molecular simulation. Jeng [8] simulated the nanoindentation process of Cu thin-film covered by polymers, with a triangular pyramid indenter. Wahab [9] and Lee [11] researched thin polymers films by nanoindentation tests. However, for these tests, the deformation details on atomic scale could not be observed, and the hardness under little indenter depth is difficult to explore. On the other hand, for simulations, little attention is spent on the atomic deformation mechanism of polymers. Since the POSS is a small
molecular, the atomic scale simulation can give the reinforcing mechanism in details. Hence nanoindentation simulations of PE and POSS-PE under three different shapes of indenters are conducted in this paper, the process of nanoindentation is analyzed in displacement, stress and energy aspects.

2. MODELS AND SIMULATION DETAILS

Strain loading is adopted in this nanoindentation. The model is shown in Fig. 2, the whole model contains two parts. The top part A is the cube-corner indenter. Another part B is the sample to test, and the bottom of B named C is fixed. The same strain is loaded on the indenter step by step.

The models of neat PE, POSS-PE and diamond indenter were built. The PE model includes 16 molecular chains. Each chain contains 498 CH$_2$ groups and 2 CH$_3$ groups. The total atom number of this model is 24032. The density is 0.904 g/cm$^3$ and the initial sizes are $a = 69.5410 \ \text{Å}$, $b = 72.2955 \ \text{Å}$, $c = 42.6211 \ \text{Å}$; $\alpha = 86.5212^\circ$, $\beta = 88.8148^\circ$, $\gamma = 103.920^\circ$. The POSS-PE model contains 16 molecular chains (Fig. 3). Each chain is built by 3 POSS monomers and straight-chain PE. The total atom number is 28448. The density is 0.97 g/cm$^3$ and the initial sizes are $a = 85.9529 \ \text{Å}$, $b = 71.6145 \ \text{Å}$, $c = 45.1090 \ \text{Å}$; $\alpha = 99.5949^\circ$, $\beta = 84.9095^\circ$, $\gamma = 72.7355^\circ$. The cube-corner indenter consists of 3469 diamond atoms. Two indentation models are formed of the three models (PE, POSS-PE and indenter), shown in Fig. 4.

In the simulations, the COMPASS force field is employed to describe the interactions between atoms. First, we optimize the structures of the models by the conjugate gradient method to get the energy-minimized structures. The indenter atoms and the bottom atoms of the sample are then fixed. After that, we start to impress the indenter under strain loading step by step. And the equilibrium states are obtained through enough relaxation each step. Gradually loading up to a certain degree, and then unload step by step. Thus, the atomic motion trajectories of the two models under loading and unloading processes are received. Note in loading versus displacement curve, the displacement is the movement distance of the indenter, and the force is the total interaction forces between indenter and sample. In all the simulations, the indenter is ideal, i.e., its shape and size remains fixable. For the two models, the displacement of indenter per step is 0.25 Å, and the total displacement is 22 Å.

3. RESULTS AND DISCUSSIONS

3.1. Load-displacement response

From the simulations of the nanoindentation, the deformation processes of the two models are visible. With the aids of the indent loading and its displacement, the loading-depth curves are depicted
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Fig. 4. (a) the initial indentation model of PE; (b) the initial indentation model of POSS-PE.

Fig. 5. (a) load-depth relation of PE; (b) load-depth relation of POSS-PE.

in Fig. 5. Clearly, several loading drop phenomena (or strain bursts) are observed. This is consistent with references [12,13]. In addition, the forces of the POSS-PE model are much larger than that of PE, which represents the deformation resistibility of POSS-PE model is stronger than PE. In other words, the resistance of PE is enhanced by incorporating with POSS.

Since the shape of the indenter is fixed, the contact area could be calculated approximatively through the contact depth. And the contact loading equals to the resultant force of the indenter due to Newton's third law. Therefore, the hardness can be obtained by

\[ H = \frac{P}{A}. \]  

According to Eq. (1), the hardness under different depths is described in Fig. 6. It is found that the hardness decreased and tended to stable value with the increasing depth. Because of the loading drops, the hardness also show some drops. After curve fitting, the hardness of PE and POSS-PE are 0.337 GPa and 0.715 GPa, respectively. Obviously, such property is improved dramatically by a factor of 1.12. Since the POSS itself has a three-dimensional structure of space with a big volume, it is hard to deform.

With the unloading curves shown in Fig. 5, the Young’s modulus can be calculated by the method of Oliver and Pharr [14]. The Young’s modulus of POSS-PE is 9.37 GPa, which is about 1.59 times larger than PE (5.89 GPa). Therefore, incorporated with POSS, the mechanical properties of PE had a greatly improvement.

3.2. Atom stress and atom average displacement near the tip of indenter

In order to interpret the enhancement effect on the mechanical properties as mentioned above, we first investigate the deformation near the tip of indenter.
Fig. 6. (a) the hardness of PE; (b) the hardness of POSS-PE.

And the atoms in the hemisphere area (as shown in Fig. 2) are considered. The center of the hemisphere is the tip atom of the indenter, its radius is \( r \). Owing to the influence of surface roughness, not the sphere, but the hemisphere is selected in this work. The absolute values of the displacements of the atoms in the hemisphere are calculated, and the average of absolute values (named “average displacement”) is used to compare the deformation of the two models. As shown in Fig. 7, the average displacements at different radius were obtained. The results indicate that the deformation of POSS-PE is much less than PE and the deformation decreases as the increasing \( r \). Such consequence proves that POSS restrains the deformation of PE.

As mentioned previously, several loading drop phenomena were found under loading. To investigate the phenomena, we observed the stress distribution of the PE model at different depths (as shown in Fig. 8). It was found that the stress near the indenter tip was bigger, and the change of stress was also mainly occurred near the indenter tip. Overall, the stress increased with increasing depths. Figs. 8b and 8c were the two states before and after loading drop. Compared with the two figures, the result showed that the purple area reduced obviously, and the green area increased. This means that the stress concentration near the indenter tip was relaxed.

For single crystal, it was believed that the main source of loading drop was collective nucleation or dislocation avalanches. Similarly, note that the slipping near indenter tip was the most important factor in load drop phenomena for polymers. To further research on the loading drop phenomena, the average displacements before and after loading drop were calculated, as shown in Table 1. Here, “Average displacement-b” is the average displacement before loading drop, while “Average displacement-a” stands for the after case. Major drop in displacement is
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found in the latter, which reveals some atoms moved back. Furthermore, the process is not unloading process but loading process, so only a part of atoms move back, not all. In other words, a part of atoms move backward, but others move forward. In the following discussions, we will show that when slipping happened between two chains, one chain contracted and moved forward, while another chain contracted and moved backward, i.e., slipping occurs in loading drop.

3.3. Slipping energy between two molecular chains

Since the loading drop was mainly caused by the slipping between molecular chains, the acuteness degree of load drop depended on how much slipping between chains. That could not be measured directly for complex polymers. Thus, slipping work or slipping energy was considered to simply quantify the slipping between molecular chains.

For the sake of simplicity, the slipping work and energy of two molecular chains were investigated. Two paralleled molecular chains of PE were built. And the degree of polymerization both was 125. As shown in Fig. 9, the atoms (labeled as atom 1 and atom 2) on the end were fixed, and the other atoms were free. To emphasize the two ends, the middle section was not displayed. In the simulation, after enough relaxation, the right fixed atom (atom 2) was stretched by uniaxial tension under displacement loading step by step. The models at different displacements were shown in Fig. 9b.

Due to the definition of the COMPASS force field [15], the interaction between two molecular chains is only Van der Waals and Coulombic potentials. The friction force between the two chains equaled to the component force, which was the sum of Van der Waals force and Coulombic force in slipping direction. And the corresponding slipping work was the product of the friction force and the distance in slipping direction.

In the case of no slipping, i.e., no work done by friction force, all the work done by external force is consequently transformed into potential energy,

\[ W_e = \Delta U + U_e. \]  \(2\)

When slipping happened, the friction force will generate the slipping work (negative value), then the potential energy is composed of both two works, i.e.,

<table>
<thead>
<tr>
<th>model</th>
<th>depth (Å)</th>
<th>Average displacement-b (Å)</th>
<th>Average displacement-a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>4.75-5.0</td>
<td>1.08</td>
<td>0.95</td>
</tr>
<tr>
<td>PE</td>
<td>9.75-10.0</td>
<td>2.44</td>
<td>1.77</td>
</tr>
<tr>
<td>POSS-PE</td>
<td>6.75-7.0</td>
<td>1.32</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Fig. 9. The structure of the model of two polyethylene chains under slipping. (a) was the initial structure, (b) was structures at different displacement. In which, (i) was the initial state, (ii) and (iii) were the two states before and after the first slipping, (iv) and (v) were the two states before and after the second slipping.
Table 2. All kinds of work and energy in slipping process.

| range | distance (Å) | $W_e$ (kcal/mol) | $W_s$ (kcal/mol) | $\Delta U$ (kcal/mol) | $U_c$ (kcal/mol) | $|U_c/\Delta U|$ |
|-------|-------------|-----------------|-----------------|----------------------|-----------------|----------------|
| i-ii  | 0~4.89      | 35.29           | 0               | 35.31                | -0.02           | 0.1%           |
| ii-iii| 4.89~4.90   | 0.10            | -26.19          | -26.84               | 0.75            | 2.8%           |
| iii-iv| 4.90~6.53   | 28.07           | 0               | 28.10                | -0.03           | 0.1%           |
| iv-v  | 6.53~6.54   | 0.10            | -26.54          | -26.54               | 0.1             | 0.4%           |

Fig. 10. (a) slipping-load relation of PE; (b) slipping-load relation of POSS-PE.

$$W_e + W_s = \Delta U + U_c,$$

where, $W_e$ and $W_s$ are external work and slipping work, respectively. $\Delta U$ is the increment of potential energy, $U_c$ is the error caused by simulation process and calculations. The former three energy, $W_e$, $W_s$, and $\Delta U$ can be evaluated directly from the simulations, while the last one $U_c$ could be obtained from Eqs. (2) and (3). All the data were shown in Table 2. $U_e$ is relative small, i.e., it could be assumed to be ignored. Therefore, the slipping energy ($W_s$) can be calculated by the external work and the increment of potential energy straightforwardly and Eq. (3) could be rewritten as follows,

$$W_s = \Delta U - W_e.$$ 

Moreover, Eq. (4) shows that the slipping energy could be obtained via nanoindentation simulation.

3.4. Slipping energy for PE and POSS-PE

The slipping energy for PE and POSS-PE at each step was calculated by Eq. (4) and shown in Fig. 10. Each protrudent slipping energy is corresponding to certain loading drop. And the absolute value of protrudent slipping energy reflects the acuteness degree of loading drop. This relationship indicates the potential cause of loading drop is due to slipping between molecular chains.

Although the slipping energy reflects how much slipping between chains, it doesn’t mean the slipping resistance. As mentioned in reference [16], they proposed that the difficulty degree of displacement bursts depended on stacking fault energy (SFE),

Fig. 11. Average slipping energy in nanoindentation.
and higher SFE leads to easier bursts. To some extent, SFE is a kind of energy density. Thus, here we introduce the slipping energy density (SED) as the criterion, like SFE. We believe that the SED could reflect the resistance. Since deformation mainly occurs near the indenter tip, slipping should arise in local area, where the stress is concentrated. We distinguish the region approximately by whether the stresses of the atoms are one order of magnitude higher than others. To compare the resistance of slipping, both slipping energy and the volume of the local (or the local atoms number) should be considered together. Hence the SED is derived by dividing slipping energy by the local volume (or the local atoms number). The average slipping energy of the two models under different depths is obtained, as shown in Fig. 11. Overall, the protrudent average slipping energy of POSS-PE was obviously less than that of PE. This means the slipping resistance of POSS-PE was stronger than that of PE. In other words, the slipping between molecular chains of PE was suppressed by POSS.

4. CONCLUSIONS

In this paper, we adopt molecular mechanics method to simulate the nanoindentation test on two models of PE and POSS-PE. Diamond cube-corner indenter is employed. Numerical simulation results show that the hardness and Young’s modulus are improved dramatically. Furthermore, average displacement and slipping model are aimed to investigate the enhancement mechanism of POSS unit. There are several issues that haven’t been resolved in the current work yet. First, only one specific configuration of POSS-PE is employed in the current work, which leads to the insufficient comparison between PE and POSS-PE. Second, the value of mechanical properties is much larger than experimental data. This may be caused by the finite size effect. Larger system with more atoms could eliminate such influence. All these will be addressed in a future work.

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