MOLECULAR SIMULATIONS OF THE UNIAXIAL TENSION ON PVDF: FROM A SINGLE MOLECULAR CHAIN TO AN AMORPHOUS CELL

Fanlin Zeng [a], Yi Sun & Yizhi Liu
[*]*Department of Astronautic Science and Mechanics, Harbin Institute of Technology, Harbin, 150001, China*

Summary In the single chain simulation, the critical fracture energy, critical bond length, critical tensile force and the elastic constant are given when the chain is stretched to break. In the amorphous cell simulation, the strain rate dependence of the stress-strain relationship, the structure deformation are provided by considering two cases that the chains will never break and are permitted to break. Some results obtained in the former simulation are applied in the latter. A novel improved method is proposed to build the cell model of PVDF also.

INTRODUCTION

Poly(vinylidene difluoride) (PVDF) is a semicrystalline polymer which is widely used in fields where chemical resistance, abrasion, and thermal stability are required. PVDF has been widely investigated since it exhibits unique pyroelectric and piezoelectric properties [1, 2] in practical applications. These properties mainly derive from the polar β phase of PVDF. A β PVDF is usually prepared by the uniaxial tension on an amorphous PVDF with very large strain (about 400%). It is very necessary and important to explore the deformation, entanglement and breakage of the PVDF chains at such a high strain. Currently, molecular simulations may be the best way for this. Although the large deformation uniaxial tension simulations of some polymers such as polyethylene (PE) have been investigated by many researchers [3], the factor of chain breakage is rarely considered.

SIMULATIONS OF A SINGLE PVDF CHAIN

The model of a single PVDF molecular chain is shown in Fig.1. A supercell with periodic boundaries is built and a single PVDF molecular chain is put in the center and along with the *z* direction of the cell. The cell width is much larger than that of the chain to avoid the influence of the neighbor mapped chains derive from the periodic boundaries. The uniaxial tension along the *z* direction was simulated using the CASTEP module in the Materials Studio software packages from Accelrys Inc. The strain loading of 0.01 on the *z* direction of the cell is added and kept at each step, and then the configuration and the energy of the chain is optimized by DFT method. Take it consideration that there is only one chain in the cell and its deformation in *x* and *y* direction is free, the energy change of the system is fully contributed from the deformation along the *z* direction. Then the tensile force of the chain can be described as [4] $F=-(\partial \Delta E/\partial \varepsilon_{zz})/d_0$. Here, d_0 is the original size of the cell in *z* direction, ΔE is the energy change of the chain and ε_{zz} is the tensile strain of the cell. Similarly, the spring constant *k* of the chain can be described as $k=-(\partial \Delta F/\partial \varepsilon_{zz})/d_0$. Here *F* is the tensile force.

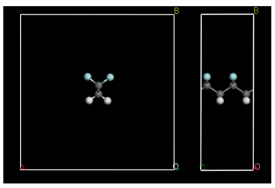

Fig.1 The simulation model of a single PVDF chain

The relationship between the energy change ΔE and tensile strain ε_{zz} of a single PVDF molecular chain under uniaxial tensile loading conditions is shown in Fig. 2. It is obviously that the chain breaks when ε_{zz} reaches to 0.30. At the step before the breakage, ΔE is 4.56 eV. From the gradients of polynomial fitted ΔE-ε_{zz} curve, forces corresponding to strain of the supercell were calculated (shown in Fig. 3). It is found that the critical tensile force is about 6.75 nN at the strain of 0.28 before the chain breaks, which means there is a slight yield process when the chain breaks down. Similarly, from the gradient of the polynomial fitted F-ε_{zz} curve, the spring constant *k* of the chain were calculated and plotted against the strain as shown in Fig. 4, which decreases with increasing strain until failure. This curve is so different from that in some famous forcefields such as DREIDING, PCFF, COMPASS, and so on, where the spring constant of a chain show an almost constant value [4]. The structures of the chain before and after the breakage are shown in Fig. 5, where the C-C bonds in Fig. 5a and Fig. 5b are 1.825 Å, 1.832 Å and 1.313 Å, 2.926Å, respectively. It is obviously that two bonds in Fig. 5b are broken and the critical bond length is about 1.84 Å.

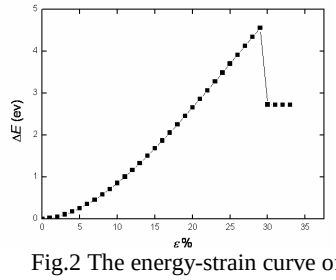

Fig.2 The energy-strain curve of a single PVDF chain under uniaxial tensile loadings

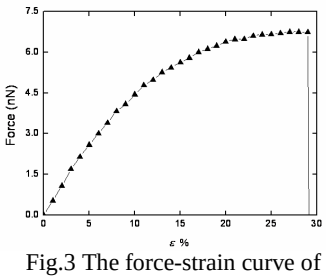

Fig.3 The force-strain curve of a single PVDF chain under uniaxial tensile loadings

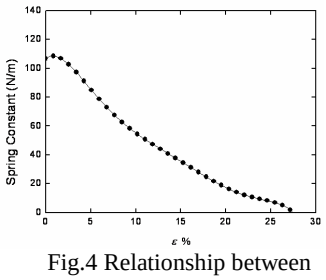

Fig.4 Relationship between the spring constant *k* and cell strain ε_{zz}

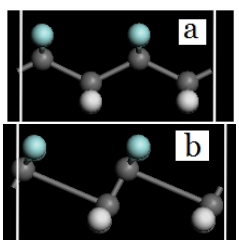

Fig.5 Structures of the PVDF chain at the strain of 0.29(a) and 0.30(b)

[a] Corresponding author. Email: zengfanlin@hit.edu.cn. Financial supported by National Natural Science Foundation of China (11102053) and the Fundamental Research Funds for the Central Universities (Grant No. HIT. NSRIF. 2010070).

THE METHOD TO BUILD AN AMORPHOUS PVDF CELL

Here we give an improved and novel method to build a large amorphous cell model of PVDF, which is very helpful to investigate the mechanics, deformations of amorphous polymers, especially for the chain entanglements, slipping and so on. Firstly, 80 PVDF chains with a relative lower polymerization degree of 200 are packed into one cuboid lattice (a=93.35 Å, b=93.35 Å and c= 120 Å) with a density of 1.60 g.cm^{-3} to build a initial cell of PVDF with periodic boundaries using the AMORPHOUS CELL module in Material Studio software. The end carbon atoms in each chain are set as active ones, which are permitted to 'react' each other to construct covalent C-C bonds. This means that relative shorter chains have a chance to catenate each other to form much longer chains. Secondly, run a molecular dynamics (MD) simulation with NVT ensemble. During the simulation, one active carbon atom is continuously searching for other active ones from different chains in the reaction cutoff distance range (10 Å here) to react until it has finished the reaction or there is always no chance to react. Here, when two chains have been reacted once their remaining active atoms are marked to avoid reacting again and producing a ring. Finally, after checking the modified cell and adding hydrogen atoms to the remaining active carbon atoms, the energy of the system is minimized to get the optimized cell structure and a NVT MD simulation is run to achieve the equilibrium cell configuration. All steps are coded as a Perl Script and run in the Material Studio software. As a result, we finally obtained a cell with 30 chains (96060 atoms), and the polymerization degree of the longest one is 2200, which means 11 initial chains have been catenated in this molecule. The cells before and after the reaction are shown in Fig. 6. It is obviously that the chains are much fewer and much longer in Fig. 6b compared to Fig. 6a.

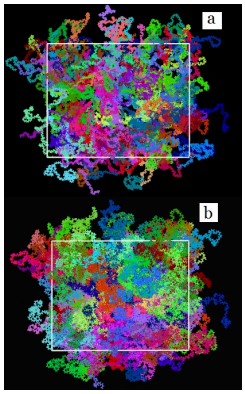

Fig. 6 The cell before (a) and after (b) the reaction among active atoms

SIMULATIONS OF THE AMORPHOUS PVDF CELL

MD simulations of the deformation in the amorphous PVDF cell as described above under a uniaxial tensile strain applied at a constant strain rate and 300 K were then performed in LAMMPS by using the PCFF force field. The end parts of the cell with 10 Å length (along z direction) were fixed and periodic boundary conditions were used in three dimensions. Strain rates of 10^{10} s^{-1}, 10^{9} s^{-1}, 10^{8} s^{-1} and 10^{9} s^{-1}, 5×10^{8} s^{-1}, quasistatic were respectively applied when chains will never break and are permitted to break. In latter case, the critical broken bond length of 1.84 Å of C-C obtained before was adopted. The maximum strains are different; vary from 0.22 to 1.0, depending on the simulation conditions. Fig.7 shows the stress-strain responses and Fig.8 shows the snapshots of the cell at some key strains, for different simulation conditions. The curves with strain rates of 10^{10} s^{-1}, 10^{9} s^{-1}, 10^{8} s^{-1} are quite similar when the breakage factor is not considered, and the stress reaches to very high value with increasing strain. But when the breakage is considered, stress drops suddenly at a low strain of about 2.1, which means the model is broken under 'impact'. A relative lower strain rate (5×10^{8} s^{-1}) only slightly delays the broken point compared to 10^{9} s^{-1}, shows these strain rate values are all too high and not suitable when the breakage is considered. Curve for quasistatic shows that one chain is likely to break up at strain of about 0.15, but the model is not broken even the strain reaches to 0.85. Structures in Fig.8 show that obvious

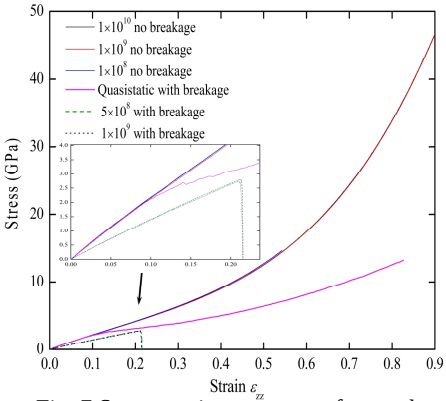

Fig. 7 Stress-strain responses of amorphous PVDF at different strain rate, with breakage and no breakage factor being considered

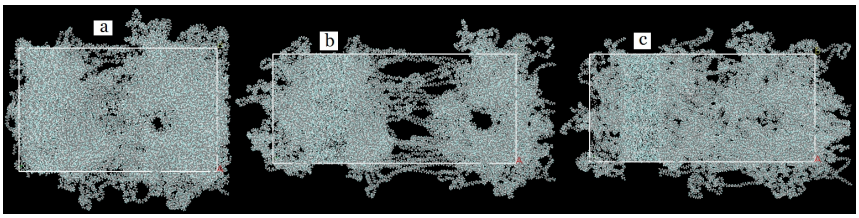

Fig. 8 Morphological change of the PVDF cell: ε is 0.34 (a) and 0.85 (b) at strain rate of 10^{9}/s with no breakage factor being considered, ε=0.85 (c) in a quasistatic simulation with breakage factor being considered

micros and craze start to appear at stain of 0.34 and strain rate of 10^{9} s^{-1}, and the craze develops very quickly with no bond breaking considered. But in a quasistatic simulation only small micro voids appear even the strain is high to 0.85. Thus the strain rate is also very important and the impact effects in high strain rate can not be ignored in the simulations.

CONCLUSIONS

Strain rate and bond breaking play key roles in tensile simulations of polymers, especially in large deformation simulations.

References

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