RESEARCH ARTICLE

Computer simulation in polymer science

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Abstract: This paper summarizes the development and current situation of computer simulation in polymer science, introduces its research methods and research fields, and points out its development direction.

Keywords: Computer simulation; Monte Carlo method; molecular dynamics; molecular mechanics

With the development of computer technology and polymer science, people are not satisfied with the use of experimental methods to develop new polymer materials and improve the performance of existing materials. Therefore, in addition to experiments and theory, computer simulation has become a solution to polymers. The third important component of practical problems in science[1]. Computer simulation is neither an experimental method nor a theoretical method. It is based on experiments and constructs a set of models and algorithms through basic principles to calculate reasonable molecular structure and molecular behavior[2]. Using molecular simulation techniques, one can have a more comprehensive understanding of the mechanisms at the atomic and molecular levels of materials.

Since the 1980s, the use of computers for the design of organic molecules and drug molecules has been greatly developed, the crystal database of the University of Cambridge, the protein database of the National Blue Haven Laboratory, and many other chemical information and data. It also provides abundant resources for the design of polymers[3]. Based on crystal database, molecular mechanics, quantum chemistry and molecular graphics techniques are combined to simulate the relationship between structure and properties of polymers[4]. MSI Corporation in the United States has made great progress in molecular simulation software, developed molecular design and application software such as Cerius 2, which greatly promoted the application of computer simulation in polymer science.

1. Computer simulation method[1,5,6]

For the structure of intact and non-holocrystalline crystals, the kinetic and thermodynamic properties can be modeled using three main methods. They are molecular dynamics (referred to as M D), Monte Carlo methods (referred to as M C) and molecular mechanics methods (referred to as M M). Among them, molecular dynamics methods have been applied to simulate atomic diffusion, cascade collision, ion implantation, melting, thin film growth, phase transformation, surface and defects, etc., can obtain atomic structural factors, state equations, elastic modulus, thermal expansion coefficient Physical quantities such as heat capacity and helium; Monte Carlo method is suitable for studying stochastic processes and phenomena in materials, mainly used to simulate film growth, diffusion, defect behavior, phase transition, collision and seepage; molecular mechanics method discusses the structural deformation of molecules from several main typical structural parameters and forces, i.e. the variation of bond length, bond angle and dihedral angle. The potential energy function of non-bond interaction is used to describe the change of internal stress or energy caused by the change of molecular structure. The 3 methods have their advantages and complement each other.

2. The application of computer simulation in polymer science

Computer simulation has been applied in all aspects of polymer science, including simulated polymer solutions,

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amorphous, crystalline, liquid crystal, blends, block copolymers, interfaces, surfaces and films, biopolymers, polymers. Local motion, rheological properties of liquid crystal polymers, mechanical properties and electrical activity. It can also help us to understand the interaction and catalytic mechanism between molecules, predict the crystal structure and mechanical properties of conformational state transitions and material properties, develop polymer elastic theory, simulate the conformation structure of polymer liquid and Raman spectroscopy[2]. In the above fields and many other fields, polymer science researchers have done a lot of fruitful work. This article only introduces the typical and latest work.

2.1 Simulation of polymer structure and properties

The modeling of crystalline polymers is much easier than amorphous polymers. For example, ideal polyethylene crystals can be modeled by first constructing an all-trans single chain and arranging them into bundles perpendicular to the length[7]. Sumpter, Noid and Wunderlich[8] simulated the structure of a single-stranded polyethylene orthorhombic crystal containing 100 repeating units containing -CH 2 - as shown in Fig. 1. The 37 active chains are surrounded by 24 fixed chains with a total of 61 chains of 6,100 atoms. Instead of using periodic boundary conditions, the outer 24 fixed chains are used as the boundary layer.

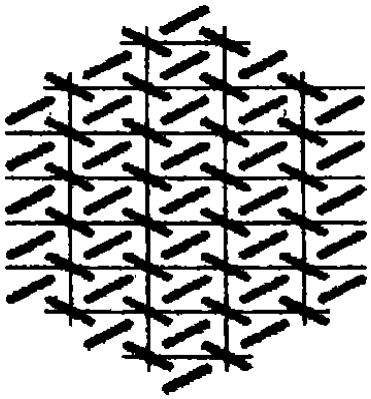

Figure 1; End view of the idealized polyethylene crystal model

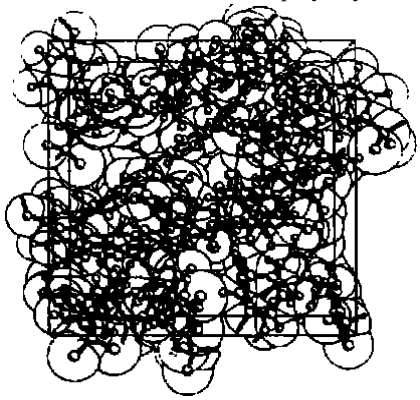

Figure 2; Energy-minimized polycarbonate structure

There are two main methods for modeling amorphous polymers, namely Monte Carlo and rotational isomerism. Suter *et al*.[9] simulated the structure of glassy bisphenol A carbonate as shown in Fig. 2. The repeating units of polycarbonate are large and complex, with six rotatable single chains, which require multiple steps of energy optimization. First, gradually increase the non-bond radius and the charged charge in the energy optimization process from the 14th to the 20th steps, and then add all the rotation barriers to increase the radius and charge to the next 13 to 20 steps of energy optimization. Normal size, the final structure is not affected by the history of energy optimization. A total of 13 structures were used for performance analysis. Performance analysis includes predictions of mechanical properties and electrical properties of polymeric materials.

2.2 Simulation of polymer kinetics and properties

2. 2.1 Molecular dynamics simulation of the crystallization process of single

chain polyethylene[10]:

The crystallization result of macroscopic polymer system is the statistical average of multi-chain system in polymer bulk. In the crystallization process, the crystallization behavior of single polymer chain is not clear. Therefore, it is very important to study the coagulation process of single-chain polymer for understanding the basic problems in polymer condensed matter physics. Rigby D[11,12] *et al*. used the M D method to study the crystallization behavior of polymers. Sundararajan[13] first studied the crystallization process of isolated (or in vacuum) single-chain and several-chain polyethylene. The simulation results show that the polyethylene can adjust the stacking structure through the diffusion of the segments and arrange them to form a platelet structure. Xiaozhen Yang[14] studied the crystallization nucleation process of the random chain of single-chain polyethylene in vacuum on the amorphous carbon surface. It was found that the polymer segment was perpendicular to the carbon surface in the formed ordered structure, which was consistent with the experiment. Chen Yan[10] *et al*. studied the crystallization process of single-chain polyethylene (SCPE) from elongated chain state in vacuum by MD simulation method. The transformation of different stages in the crystallization process was characterized by energy parameters and structural parameters, and their physical significance was discussed. It is found that the ordering behavior of the second stage can be described by Av rami equation commonly used in crystallization experiments.

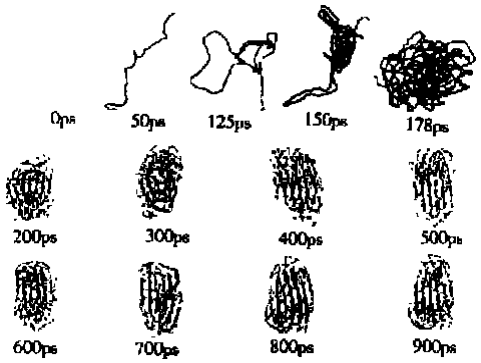

Figure 3; Time evolution of change in the shape of a polyethy- lene chain with 800 CH2 units, at 300 K

2. 2. 2 Kinetic simulation and analysis of free radical graft copolymerization[15]:

In the process of free radical grafting, a graft copolymer is formed, often accompanied by some side reactions, and a large amount of homopolymer is formed. Since the homopolymerization process is complicated, it is difficult to determine its mechanism and it is impossible to conduct research using conventional kinetic methods. Changmian[15] *et al*. investigated the typical graft copolymerization process by computer simulation. Firstly, starting from the connotation law of variable correlation function, the curve model in the sense of Tchebycheff was simulated in Euclid space, and the best approximation was made to the homopolymer part in the process of copolymerization. The method is based on the regression simulation of the data, and the most realistic depiction of the monomer change is obtained. On this basis, the graft initiation process is processed, and then the chain growth is induced into vector analysis in n-dimensional linear space. The Laolace transformation is used for recursive processing, and the dynamic process expression of graft chain growth including chain transfer is introduced. This provides microscopic information on a range of graft kinetics.

2.2.3 Mo nte Carlo simulation of phase separation kinetics of polymer concentrated solution[16]:

In recent years, the theoretical and experimental research of phase separation kinetics has become a new hot spot in the international academic community[17–22]. Existing numerical calculations[20], cellular dynamics simulation[21] and other methods can well describe the phase separation process of binary copolymers, but can not deal with the chain conformation problem in detail; the molecular dynamics simulation is too fine, so the simulation efficiency is extremely low when dealing with multi-chain systems. The Mo nte Carlo method based on chain dynamics simulation[22], although fluid dynamics interactions cannot be considered, can simultaneously examine the two levels of phase behavior and

chain conformation. The method has been successfully applied to study the phase equilibrium of polymer blends and block copolymers[23], and the shortcomings of Flory-Huggins mean field theory[24] are pointed out. Binder *et al*.[25] also used Mo nte Carlo simulation to study the phase separation kinetics of a two-component polymer with symmetric molecular weight. Xu Guoqiang *et al*.[15] used the chain dynamics Mo nte Carlo method to simulate the kinetics of spinodal phase separation of polymer concentrated solution. The results show that the position of the scattering peak shifts to the left in the early stage of phase separation, which does not conform to the classical Cah n-Hilliard linear theory; At the later stage of phase separation, the morphology of polymer phase is percolated, and the structural factors can be scaled, and basically conform to the corresponding Fu-rukawa scaling law. The simulation results are consistent with the related experiments. It is suggested that the size of the coil shrinks sharply at first and then rises gradually with the phase separation. The results show that the M onte Carlo method can simultaneously investigate the conformational change of the polymer chain and the phase separation process of the multi-chain system as well as their correlation.

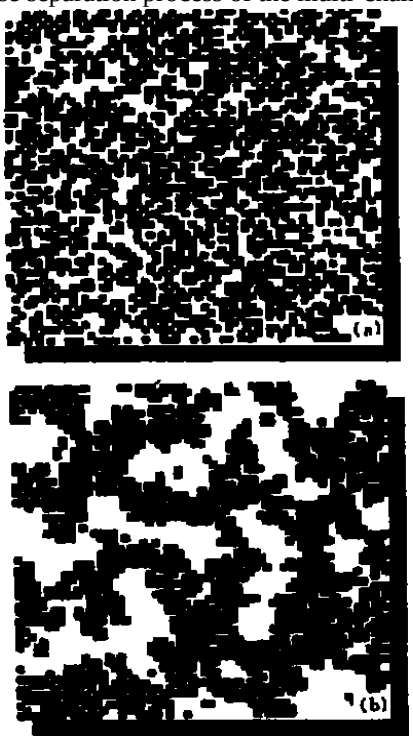

Figure 4; The ins tantaneous phase morphology during phase sep- aration of polymeric dense solution

(a) t= 0, initial s tate; (b) t= 5000 ps, phase seperatings tate

2.3 Computer simulation of polymer applications

2.3.1 Application of Molecular Simulation Technology in Oilfield Chemistry[26–30]:

Auxiliary oilfield chemical molecular design and study of the microscopic nature of some macrochemical problems in oil and gas exploration, for example, simulate the growth and surface morphology of carbonate compounds, study the hydration treatment of clay minerals, study the internal structure of micelles, study the stability of natural gas hydrate, study the conformation of polyelectrolyte in solution and adsorption on mineral surface, simulate the deposition of wax and asphalt, etc. The calculation of scale remover and cement slurry coagulant can be realized by using CERIU S2 software package of MSI company. The mineral samples can be quantitatively analyzed by X-ray diffraction data. DM O L, POLYM ERIZED and DISCOV ER modules of BIO SYM IN SIGHT II software can be used to study oil field chemical problems such as metal corrosion, polymer degradation, adhesion of petroleum components to mineral surfaces, clay stability, viscosity control and fire fighting wax.

2.3.2 3D RTM Filling Simulation[31]:

The numerical analysis of the filling process began in the late 1970s and can be divided into three stages, namely, the early one-dimensional and simplified two-dimensional, medium-term complex two-dimensional and current three-dimensional[32]. Ren Shijie *et al*.[31] used a mixed numerical method to numerically simulate the three-dimensional

RTM filling process, that is, using the finite element method in the cavity width direction and the finite difference method in the thickness direction to solve the three-dimensional problem. Avoid the difficulties caused by directly seeking three-dimensional finite elements. At the same time, any Lagrangian-Eulerian method is used to process the flow front, and the numerical results are discussed.

2.3.3 Computer simulation of the rupture process of uniaxially stretched composites[33]:

Hedg epeth's shear lag model is usually used to calculate the stress concentration factor when performing Monte Carlo simulations. The shear lag theory approximates that the fiber is subjected to tensile stress and the matrix transmits shear stress. This assumption applies only when the matrix tensile stress has a small effect on the composite, ie Ef /Em and Vf /Vm are higher. On the basis of proposing a new composite model, Hu Pei *et al*. deduced the equation of strain concentration coefficient, and then simulated the influence of the fracture process of uniaxially stretched composites by Monte Carlo method. The new model is more in line with the situation.

3. Conclusion

Computer simulation technology, widely used in polymer science, is constantly evolving and improving as a tool for modern scientific research and development. At present, the speed of the central processing unit of the computer is constantly increasing, the memory of the computer is constantly increasing, and the speed of the computer bus is continuously increasing. All of this has led to a qualitative improvement in the overall functionality of the computer and has also contributed to the development of computer graphics, making computer simulations easier to observe and easier to understand. Moreover, the computer has created a virtual reality, the results of which can be expressed not only by computer graphics, but also by the five senses. At the same time, with the increase of the complexity of the polymer system studied, higher requirements are put forward for the algorithm itself. We are convinced that with the development of polymer science and computer simulation methods, the application of computer simulation in polymer science will be more and more promising.

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