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Molecular dynamics study on polymer filling into nano-cavity by injection molding

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ABSTRACT

Injection molding is one of the cost-effective technologies to produce polymer items towards mass production. In nano-injection molding, the final replication quality of nanostructures is strongly dependent on the filling quality in nano-cavities. In this paper, simulation models for polymer filling into nano-cavities were constructed to investigate the effects of molecular weight and cavity size. The glass transition temperature of isotactic PMMA with different molecular weights was calculated. Characteristics of configuration and snapshots during the filling process were analyzed. Density distribution, velocity profiles and mean-square gyration radius were proposed to investigate the filling quality and the flow behavior. Simulation results showed that the calculated glass transition temperature was higher than the experimental result and increased with the molecular weight. The filling behavior and final replication quality were highly depended on the molecular weight and the cavity size. A higher density distribution was observed in the edges along the nano-cavity by the nonbonding interactions. During the filling process, the gyration radius was firstly decreased rapidly, and then went up to approach the initial value. Atoms in central area exhibited the highest flow velocity, while the velocities of atoms were gradually decreased with the distance from the center.

1. Introduction

Nano-manufacturing technology, as one of the most potential technologies in the 21st century, is an essential foundation to support components towards application [1]. Polymer products with nanostructures are widely used in biomedical, information storage, flexible electronics and other fields, such as nanofludic chips, light extractions in light emitting diode (LED), and thin-film solar panels [2–4]. Among all the nano-manufacturing technologies, nano-molding technology is an effective method for mass-production of nanostructures. This top-down method mainly includes LIGA (German for Lithographie, Galvanoformung and Abformung), hot embossing and nano-imprint lithography [5–8]. Injection molding is regarded as one of the cost-effective technologies to produce polymer items towards mass production. Sub-micrometer/nanometer surface structures have been successfully fabricated by injection molding in recent years [9,10]. Researches nowadays are focusing on the challenges of how to produce nanostructures with higher aspect ratio or smaller pattern size [11,12]. During the injection molding process, the final replication quality of nanostructures is strongly dependent on the filling quality in nano-cavities. A better understanding of flow behaviors during the filling process would be essential to the design of products with nanostructures.

Analytical methods have been done to investigate the flow behavior and the replication quality in micro injection molding. Recently, analytical results have provided valuable information for the polymer flow behavior but also presented some limitations for the analysis of micro-scale system [13–15]. When the system of consideration becomes smaller than several tens of nanometers, continuum mechanics fails to predict the system behavior because material properties changes drastically in nano-scale compared with those in macro-scale [16]. If the scale of nanostructures is down to the size of just one molecule, due to the obvious particle characteristics and other scale effects, the flow behaviors are highly affected by the surface tension, nonbonding interaction and the movements of macromolecules during the injection filling process. Molecular dynamics is a computer simulation method for studying the physical movements and interactions of atoms and molecules, and it has attracted wide attention for the analysis of nano-scale systems.

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Nowadays, molecular dynamics method has been widely used to analyze the flow behavior in nano-system [17,18], interface interactions [19,20], thermal conductivities [21,22], nanometric cutting [23,24], nano-imprinting lithography [25–29], etc. Molecular dynamics studies on the filling process of injection molding nanostructures, however, were rarely reported. Despite the huge gaps of timescale between the molecular dynamics method and experimental research, the molecular dynamics simulation can provide qualitative estimation of flowing behaviors at the nanoscale [30]. For these gaps and the time–temperature superposition principle, the time span corresponding to the temperature variation in practice is too short to distinguish the resulting differences in simulation. The same does other processing parameters. The processing parameters in practice would thus be not the main objectives in molecular dynamics simulation.

The main purpose of this paper is to propose a better understanding of flow behaviors and movements of polymer molecules during the filling process of nanostructures in injection molding. In this study, molecular dynamics simulation models for injection molding of nanostructures were constructed. The T_g of isotactic PMMA with different molecular weights was calculated. The force field was verified by comparing the calculated results of T_g. The effects of molecular weight, cavity width and cavity depth on the filling process of polymer molecules were investigated respectively. Configuration and snapshots at different filling stages in PMMA layer were analyzed. In addition, certain molecules were marked to observe the trajectory during the filling process. Density distribution, velocity profiles and mean-square gyration radius were introduced to investigate the filling quality and the flow behavior of PMMA molecules.

2. Simulation model and methodology

2.1. Model constructing

The simulation model is shown in Fig. 1. The model is in a cuboid of 7.5 nm × 7.5 nm × 17.5 nm. It consists of a mold insert layer, a PMMA layer and a vacuum layer. The mold insert layer is composed of nickel atoms, which has FCC structure with (100) plane. One rectangle nano-cavity is located in the upper of the nickel layer. The depth and the width of nano-cavity are varied from 1.5 to 6.0 nm. Isotactic poly(methyl methacrylate) (PMMA) is selected as the injection molding material. The PMMA layer is constructed in a configuration with 2000 MMA monomers in total. The molecular weights of each PMMA system are 200, 1000 and 5000, respectively. Degrees of polymerization are correspondingly 2, 10 and 50. The initial density of PMMA layer is set to be 1.18 g/cm^3 and the initial temperature is 298 K. Periodic boundary conditions in the model are selected for approximating a large system. Vacuum layer, with a thickness of 2.0 nm, is set on the top of the simulation model. In order to get access to the actual processing condition, energy minimization and anneal treatment of PMMA layer would be done to optimize the molecular structure.

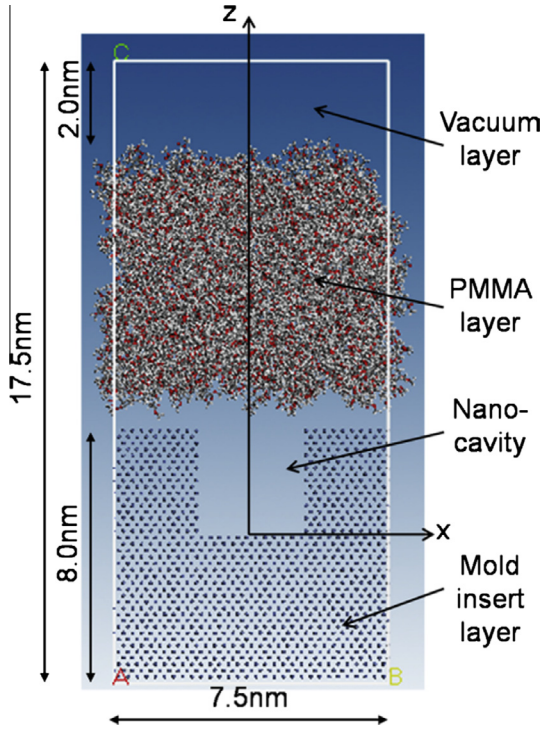

Fig. 1. Atomistic model of analysis.

2.2. Force field

The consistent valence force field (CVFF) is adopted to represent the intermolecular and nonbonding interactions between atoms in PMMA layer. It consists of bond stretching potential, angular bending potential, torsion potential and nonbonding interaction. Lennard-Jones 12–6 potentials are adopted to describe the nonbonding interaction between the atoms in PMMA layer and the nickel atoms in mold insert layer, as shown in Eq. (1).

$$\begin{aligned} U_{total} &= U_{bond} + U_{angle} + U_{torsion} + U_{nonbond} \\ &= k_b(r - r_0)^2 + k_a(\theta - \theta_0)^2 + k_t(1 + \cos(n\phi - \phi_0)) \\ &\quad + 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \end{aligned} \tag{1}$$

where the k_b, k_a, k_t and ε are constants of bond stretching potential, angular bending potential, torsion potential and nonbonding interaction, respectively. Parameters are derived from the lattice constant and adhesive energy of the nickel atom. The cutoff distance of the nonbonding interaction is set to be 1.25 nm.

2.3. Glass transition temperature

In nano-injection molding experiments, mold temperature is suggested to be maintained above the glass transition temperature (T_g) of the processed materials [31,32]. Short shots in nano-cavity and bad replication quality of nanostructures would appear when the mold temperature is lower the T_g. Because of the time–temperature superposition principle, the simulation result of T_g by molecular dynamics is higher than the experimental value [33]. In order to construct a more reliable simulation model, the T_g and the glass transition process should be recalculated by molecular dynamics method. Moreover, the calculation of T_g could be used to verify whether such structure and force field of polymer were appropriate for further simulations [34].

2.4. Simulation procedure

For T_g calculation, free-volume theory presented by Fox and Flory is used in molecular dynamics simulation. PMMA system with isotactic configuration is performed by gradually cooling process in a constant particle number, pressure and temperature (NPT) ensemble. The value of system pressure is set as a constant of 1 MPa. The PMMA is cooled down from 520 K to 200 K with a time step of 0.2 fs and a total simulation step of 100,000 steps.

Prior to the injection molding process, polymer particles should be heated to the melt temperature. In the study, PMMA layer was first heated up to the melt temperature of 500 K and then relaxed at 500 K for 50 ps in a constant particle number, volume and tem-