Available online at www.sciencedirect.com

ELSEVIER

Polymer 46 (2005) 9423–9433

polymer

www.elsevier.com/locate/polymer

Use of molecular dynamics to investigate polymer melt–metal wall interactions

Uğursoy Olgun*, Dilhan M. Kalyon

Department of Chemical, Biomedical and Material Engineering, Stevens Institute of Technology, Castle Point Station, Hoboken, NJ 07030, USA

Received 6 June 2005; accepted 14 July 2005
Available online 10 August 2005

Abstract

The classical boundary condition of fluid dynamics, i.e. the no-slip condition is violated during the flow of various complex fluids including polymer melts and polymeric suspensions. It is recognized that the dynamics of the behavior of the macromolecules at the wall, their adsorption, and disentanglement from each other and from the wall all play significant roles during shearing and flow. During wall slip it is not clear whether the macromolecules detach from the wall (adhesive failure of the slip condition) or whether the macromolecules remain tethered to the wall but disentangle from the neighboring macromolecules (cohesive failure). In this study, we seek to shed light to the basic mechanisms of the wall slip of polymers by focusing on the dynamics of the polymer behavior at the wall for three polymers, two of which exhibit significant strong wall slip, high density polyethylene (HDPE) and poly(dimethylsiloxane) (PDMS), and one which does not exhibit wall slip under typical extrusion conditions, i.e. a block copolymer BAMO/AMMO, (crystalline blocks of poly(3,3-bis(azidomethyl)-oxetane), BAMO, and amorphous blocks of poly(3-azidomethyl)-3-methyl-oxetane, AMMO). The cohesive energy densities of the three polymers were found to be in the same range, with the cohesive energy density of BAMO/AMMO being slightly higher than those of the other two. The molecular dynamics based cohesive energy density values compared well with calculations based on the determination of the group molar attraction constants. On the other hand, the energy of adhesion value exhibited by the copolymer BAMO/AMMO/iron oxide is significantly higher than the energy of adhesion values for the iron oxide/PDMS and iron oxide/HDPE systems. Considering that over the same broad range of shear stresses the block copolymer BAMO/AMMO does not exhibit wall slip and the other two polymers HDPE and PDMS do, these findings suggest that at least for these three polymers wall slip is more likely to occur on the basis of an adhesive failure mechanism.

Keywords: Polymer-metal adhesion; Molecular dynamics; Polymer melt

1. Introduction

Ab initio or molecular dynamics (MD) based simulations of macromolecules have great technological importance since they often provide a detailed understanding of many flow processes, which especially occur at solid interfaces. A wide variety of materials and interfaces have been simulated so far. For example, the molecular dynamics, MD, simulation techniques were employed by Abloo et al. in their investigation of the interfaces between the polymeric electrolytes and the electrodes [1]. For the V_2O_5 electrode and a polyethylene oxide electrolyte targeted for the Li-ion battery, they have shown that the dynamics of the motion at the solid/polymer interface is controlled by interactions between the ether oxygen of the PEO polymer and the V=O bonds of the metal. In another application, the heat of mixing values of various blends of polymers were investigated to determine if pairs of polyethylene oxide, polypropylene and polyacrylic acid were miscible or not [2]. In yet another application, Karthigeyan and Myerson have investigated the nucleation and the crystallization of isotactic polypropylene in the absence and presence of a nucleating agent using molecular dynamics simulations [3]. The results were found to be in good agreement with the experimental observations. The interactions of hydrocarbon clusters representing polyethylene with Al, Cu, and Zn were studied using an ab initio atomic cluster model and stronger

---

* Corresponding author. Address: Department of Chemistry, Sakarya University, Mithatpaşa, Sakarya 54100, Turkey. Tel.: +90 264 346 0378; fax: +90 264 346 0371.
E-mail address: ugursoyolgun@yahoo.com (U. Olgun).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.042

interaction (greater potential energy) was observed for hydrocarbon–Al interface in comparison to the interactions of the hydrocarbon cluster with the other metals [4].

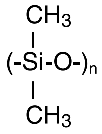
Molecular dynamics calculations have also revealed that the variations in the solid-wall and fluid interaction affect the distribution of the density of the fluid adjacent to the wall, leading to changes in the viscosity of the fluid [5]. The motion of nanoparticles confined in nanochannels has also been investigated and the motion of the particle at the wall is observed to be a slip-stick flow as affected by the interaction parameter between the wall and the fluid [5].

The present investigation was initiated upon the observation that the violation of the no-slip boundary condition during the flow and deformation of polymer melts is affected by the nature of the interface formed between the metal and polymer [6–12]. Furthermore, we have recently determined that given a wall material of construction, some polymers exhibit a catastrophic failure of the no-slip condition, while some others exhibit the no-slip condition over a broad range of shear stresses and shear rates during flow[13]. In this study, it was determined that PDMS and HDPE do exhibit strong wall slip in simple shear flows (upon the wall shear stress reaching the critical wall shear stress values of 0.2 and 0.07 MPa, respectively [13]), whereas BAMO/AMMO block copolymer does not exhibit a catastrophic failure of the no-slip condition at the wall of the rheometer with stainless steel fixtures over a broad range of shear stress values [13]. Thus, a good starting point for understanding of the fundamentals of the interaction between the metal surface and the polymer melt appeared to be the carrying out of molecular dynamics calculations of the same polymers with a typical material of construction for the wall (oxidized iron surface).

The BAMO/AMMO is a recently developed elastomer and its chemical structure is given below along with the other polymers of the study:

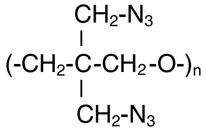
$(\text{-CH}_2\text{-CH}_2\text{-})_n$

HDPE



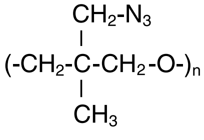
$$\begin{array}{c}\text{CH}_3\\ |\\ (\text{-Si-O-})_n\\ |\\ \text{CH}_3\end{array}$$

PDMS



$$\begin{array}{c}\text{CH}_2\text{-N}_3\\ |\\ (\text{-CH}_2\text{-C-CH}_2\text{-O-})_n\\ |\\ \text{CH}_2\text{-N}_3\end{array}$$

BAMO



$$\begin{array}{c}\text{CH}_2\text{-N}_3\\ |\\ (\text{-CH}_2\text{-C-CH}_2\text{-O-})_n\\ |\\ \text{CH}_3\end{array}$$

AMMO

The BAMO fraction is crystalline and the AMMO fraction is amorphous, thus generating a thermo plastic elastomer with BAMO hard blocks and AMMO soft blocks.

2. Molecular dynamics (MD)

For the molecular dynamics calculations, a commercially-available source code, Cerius^2 of Molecular Simulation Incorporated of San Diego, California was used [14]. Macromolecules were generated using the Amorphous Builder module with periodic boundary condition and then relaxed using energy minimization procedures. Both constant *NVE* (constant volume, energy and number of atoms) dynamics and constant *NPT* (constant pressure, temperature and number of atoms) simulations were performed. The cell size was taken to be more than twice the van der Waals radius in order to avoid the periodic nature of the model fluid [3]. The Dreiding force field (a purely diagonal force field with harmonic valance terms and a cosine-Fourier expansion torsion term) was used for the calculations [15]. The van der Waals interactions were calculated from the Lennard–Jones potential. Electrostatic interactions were described by atomic monopoles and distance-dependent Coulombic term. Hydrogen bonding is calculated by an explicit Lennard–Jones 12–10 potential. During the simulations, the following specific procedure was employed.

2.1. MD simulation of polymer melts

1. Following Karthigeyan and Myerson, the typical model for the simulation employed the use of four polymer chains (the number of backbone atoms in each chain were 90 for HDPE, 90 for PDMS and 80 for BAMO/AMMO), which were all in their random configurations [3]. The Amorphous Builder module of the software was employed to represent the macromolecules in molten state [14]. The four chains were taken to represent the bulk state of the polymer melt in conjunction with a 3D periodic system.
2. In the 3D periodic system, a cube of typical side length of 30–40 Å was constructed to contain the four chains at the desired density value (initially low). A bump-checking algorithm was used to control how close the nonbonded atoms of the molecules could come together. In this procedure, the allowable distances pertain to the van der Waals radii of the two atoms, r_0, multiplied by the van der Walls scale, R [14]. A value of $R=0.89$ is taken for the maximum value of the distance at which the potential energy U becomes equal to zero, i.e.:

   $$U(0.89r_0) = 0 \tag{1}$$

   This is the distance at which the Lennard–Jones 12–6 potential becomes repulsive [14]. A default value of $R=0.3$ was used in our simulations.
3. The stable conformations of the macromolecules (for which the net force on each atom vanishes) were determined by the adjustment of the atomic coordinates