The diffusion of an antifoulant in an equilibrium swollen P(MMA-*co-n*-BMA): A molecular dynamics simulation study

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ABSTRACT

In the past decades, the poisonous residues of antifouling (AF) paints have become an urgent issue in the marine AF industry, which have driven the development of improved AF technology. Controlled release is an effective method to decrease the diffusion of the penetrant within a polymer but has not yet been applied in the marine AF field. In this paper, molecular dynamics (MD) simulation was performed to analyze the diffusion of 4,5-dichloro-2-*n*-octyl-4- isothiazolin-3-one (DCOIT, antifoulant) in P(MMA-*co-n*-BMA) immersed in water. The glass transition temperature (Tg) was simulated in the dry and equilibrium swelling (ES) states, and the dynamics of water in the ES state and the free volume were investigated. The diffusion mechanisms of DCOIT were also analyzed. The results show that the water space and the free volume create large channels or paths for DCOIT transport and that the diffusion of DCOIT can be controlled effectively with water and Tg as the crucial factors. Furthermore, the diffusion ability of DCOIT is significantly enhanced when the swollen matrix is in the rubbery state.

1. Introduction

Biofouling, *i.e.*, biological colonization or settlement, has serious adverse effects on submerged man-made surfaces that are in contact with marine water, resulting in significant economic costs in the maritime industries [1]. The most widespread solution to minimize the effects of biofouling, is to coat the immersed surfaces of these structures with biocidal antifouling (AF) paints [2]. Unfortunately, investigations in coastal water have shown that these biocidal substances (*e.g.*, tributyltin, a metal-based organotin compound) have caused a series of environment problems because of their high toxicity and chemical stability, leading to ecological disturbance [3]. Thus, legislation has resulted in global limitation of the application of tributyltin since January 2003 [4], spurring an increased interest in research on non-toxic alternatives or methods. Synthesized chemical substances, the toxicity of which can be eliminated by induced degradation, have received considerable attention as environmentally friendly antifoulants [5]. However, because of the conflict between their relatively high solubility and the low values of the effective release rate, these chemicals have been limited in their application. For example, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOIT), the core component of

Sea Nine 211, which won a Presidential Green Chemistry Challenge Award in 1996 for its excellent AF performance, has a high solubility of 14 mg/l, but the effective release rate is as low as 2.9 μg cm^{-2} day^{-1} [6], a significant gap that might result in premature depletion in the coating and reduce the lifetime of the AF coating, as well as increasing the AF cost. Traditionally, improving the performance of an AF coating involves minimizing the solubility and the effective release rate of the antifoulant. Many methods have been proposed to address this challenge. For example, some studies have reported advancements in the controlled release of antifoulants by encapsulation techniques [7,8]: both metal antifoulants [9,10] and organic antifoulants [8,11–13] were used, and these technologies were demonstrated to indeed achieve the anticipated decrease in the release rate and to enable a moderate leaching rate of biocides. Hoffman [14] proposed an innovative idea in which multiple types of stimuli and responses associated with existing "smart" polymers were introduced into an AF coating. However, further progress in the controlled release of antifoulants and its practical application has been hindered by the lack of fundamental understanding of the diffusion of AF agents and of the physico-chemical properties of the swollen polymeric matrix, as well as by the high cost.

In essence, research on the controlled release of an antifoulant

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belongs to the field of molecular diffusion, which depends on the physical structure of the matrix and on the ambient temperature. Early theoretical studies in this area primarily employed two theories, *i.e.*, the free volume approximation [15,16] and transition-state theory (TST) [17,18], to explain the diffusion of the penetrant molecules in a polymeric matrix [19]. In the free volume approximation, the hole free volume in the polymer acts as a tunnel to transport the molecules and its redistribution would move the penetrant molecules because such redistribution requires negligible energy; however, the transportation would depend on whether the hole is large enough to host a penetrant molecule. In TST, the diffusion of the penetrant is treated as a unimolecular rearrangement in which the penetrant moves from an initial cavity to a saddle point and then to a neighboring cavity. Therefore, the reaction trajectory in configuration space is tracked and the transition rate constant is evaluated. This method has been used to calculate the diffusion coefficient of a low-molar-mass substance through a polymer matrix [18]. Both of these two theories are limited to investigating the diffusion of a single penetrant in a simple polymer system, while problems arise when analyzing the diffusion of multiple penetrants or complicated systems (*e.g.*, a swollen matrix containing multiple kinds of penetrants) because of the lack of defined parameters. In contrast to light gases (or low-molar-mass substances) and ionic liquids [19,20], most organic antifoulants are crystalline with molecular mass in the hundreds of g/mol. Therefore, they have low self-diffusion ability because the thermal motion is fettered by the crystal lattice energy. The diffusion of organic AF molecules in a polymeric matrix is difficult to determine experimentally. Moreover, there are no reports investigating the diffusion of AF agents at the molecular level or demonstrating the mechanism of their controlled release. Therefore, understanding of the microstructure of the swollen polymer and water by experimental methodologies remains elusive.

In molecular dynamics (MD) theory [21], the trajectories of atoms or molecules are determined by numerically solving Newton's equations of motion, where the forces between the atoms and their potential energies are described using molecular mechanics force fields. The interaction of the atoms or the molecules is depicted in a fixed period of time, providing a view of the dynamical evolution of the system without considering the macro state. MD simulation, a combination of computer technology and MD theory, has become a powerful tool in materials science to bridge the gap between macroscopic experiments and the microscopic molecular movement of the swollen matrix and the diffusion of small molecules within it [22]. Therefore, the length of the trajectories can be described on the order of nanoseconds depending on the calculation capacity, and thus, the diffusion of the penetrant molecule in the polymeric matrix and the structural properties can be studied in detail. As a result, a kind of multiple-factor study including the water/matrix, pendant group/water, water/penetrant (small molecules), and penetrant/matrix interactions can be carried out by examining the molecular motion. For example, Tung et al. [22] simulated gas transport through PMMAs of different tacticities, and they found that the distinct tacticity types gave different Tg values for the two types of PMMAs and that the former species had lower flexibility and longer chain conformations than the latter species. Bharadwaj [23] simulated the diffusion of N_2 within PMMA with different water contents and revealed the effect of the H_2O concentration on the static free volume of the PMMA. Smit and Mulder [24] found three types of motion mechanisms by simulating the motion of light molecules in polyimide membranes: jumping motion, continuous-motion and trapped motion. Similar motion was also observed in the diffusion of oxygen and nitrogen gas within polyether ether ketone (PEEK) membranes [25]. Shingo [26] investigated the structure of the water cluster in a swollen perfluorinated ionomer and found that a stable water path exists in a highly humid membrane with 20 wt % water content, while the dynamic formation and destruction of continuous water clusters occur at relatively low humidity. The combination of the volume expansion and the existence of a water path in the swollen matrix, suggests the

possibility that larger molecules could diffuse in the polymer matrix. Additionally, Jhon and Andrade [27] first proposed a "three-state model" for water in a swollen polymer. In this model, the three states are bound water (BW), loosely bound water (LW) and free water (FW). These three water structures have been confirmed experimentally [28] and theoretically for a PSiMa-IPN-PMPC hydrogel [29] and perfluorinated ionomer [26] by MD simulations. Obviously, LW and FW would contribute to the formation of the water path, while BW would bind with the polar groups. These studies provide significant support indicating that the diffusion of some large penetrant molecules in a swollen but dry matrix might contribute to the formation of a water path, which can host a penetrant molecule.

Based on previous results, in this work, we simulate equilibrium swollen matrixes by atomistic MD in a narrow temperature range and investigate the diffusion of antifoulant molecules in the matrixes. DCOIT, the molecular mass of which is 282.23, is selected as the model organic antifoulant. First, the second-order phase transition (Tg) of the amorphous polymer in the dry and swollen states is calculated. Next, the equilibrium swelling (ES) systems are investigated by analyzing the dynamics of the chain and water and the water distribution in the swollen polymer. On this basis, the diffusion of the antifoulant in the ES state is further analyzed. The conclusions are summarized in Section 4, which also describes the main outcomes of this study and the outlook for future directions in research on the controlled release of DCOIT.

2. Theoretical models

2.1. Model construction

Simulation is performed in the Materials Studio 6.1 software, and the COMPASS force field is used to determine the potential interactions of the atoms in the systems. The simulation system in this work consists of P(MMA-*co-n*-BMA), water and DCOIT (the antifoulant molecule). The three components are constructed in Polymerizer. Three structures of P(MMA-*co-n*-BMA) with different ratios of MMA and *n*-BMA, *i.e.*, 50:50, 40:60 and 30:70 (M50B50, M40B60 and M30B70, respectively) are used because MMA and *n*-BMA have reactivity ratios of 0.926 and 1.027, respectively, and show identical reactivity in free-radical polymerization. Therefore, the constructed P(MMA-*co-n*-BMA)s can, in principle, reflect the structure resulting from free-radical polymerization. The periodic cell contains one P(MMA-*co-n*-BMA) chain consisting of 100 units, while the swollen P(MMA-*co-n*-BMA), including the ES state, are constructed by the insertion of a different amount of water into the Connolly surface area of the periodic cell, according to our former publication [30]. The flexible TIP3P model is applied for water. Intermolecular interactions are modeled with the Lennard-Jones 9-6 (L-J 9-6) potential and Coulombic interaction. The *VDW* interactions are computed with an atom-based cutoff distance of 15.5 Å to obtain an accurate result, and the Ewald summation method is used to calculate the electrostatic interactions with an accuracy of 0.001 kcal mol^{-1} [31,32]. Long-range energy correction is considered. All systems are set to be neutral.

All MD simulations are performed at 0.1 MPa with periodic boundary conditions, the Berendsen method is utilized for pressure control, and a Nosé-Hoover-Langevin (NHL) thermostat is used to control the temperature of the system. The motion equations were integrated with the Verlet leapfrog integrator [33]. The detailed simulation process is reported in our previous publication [30]. The simulations are performed in three steps. In the first step, energy minimization is performed using the smart method with an initial step size of 0.0005 nm and adaptive step-size control until the maximum force change on each atom is less than 0.05 kJ/(nm.mol). In the second step, MD equilibration is performed with variable and constant temperature in an isobaric-isothermal (*NPT*) ensemble to optimize the conformation until the density remains stable within normal volume fluctuations. The variable temperature is in the range from 300 K to 600 K, and the