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Two-phase molecular dynamics model to simulate the migration of additives from polypropylene material to food

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ABSTRACT

Migration of chemical additives from polypropylene material to food simulants (50% ethanol solution and isooctane) at the temperature of 293, 313 and 343 K are investigated by using molecular dynamics (MD) simulation technique based on the classical mechanics. A two-phase MD model is firstly established to simulate the migration dynamic process. The migration dynamic details are obtained, especially for the significant kinetic parameter of diffusion coefficient. The accuracy of MD simulation is assessed by comparing the diffusion coefficients obtained by MD simulations, experiments and Piringer model. It is indicated that the diffusion coefficients of additives obtained from two-phase MD model are generally within one order of magnitude of the corresponding experiments. The two-phase MD model of polypropylene – food simulant offers fairly good predictive ability, which means MD simulation technique is a powerful way to predict the migration process and level of additives from polypropylene material to food. In addition, different influencing factors for additive migration are examined including the additive molecular structure, interaction energy between additive molecule and polypropylene, food simulant and temperature. The movement trajectories of additives in polypropylene – food simulant cells at different simulation time suggest that the additive molecules vibrate rather than hopping for a long time, until they find the equal or larger transport channel to diffuse.

1. Introduction

In the last decades, polymer materials are widely used to package food because of their advantages including easy shape formation, durability, lightweight, recyclability, and transformability. During the manufacturing process of polymer materials, additives such as antioxidants, light stabilizers, plasticizers, and others are incorporated to improve and preserve the properties of polymer [1]. When the polymer packaging is in contact with food, the additives initially dispersed in polymer may migrate into food, the food molecules are also able to migrate to polymer and make impacts on the performance of polymer material [2,3]. This is a mass transfer process. Some additives are known to be potentially carcinogenetic to humans and endocrine disruptors [4,5]. So, assessment of consumer's exposure to additives originated from polymer materials is very important.

Diffusion coefficient is a significant kinetic parameter and plays a crucial role in determining the migration level of additives from polymer materials to food under specific storage conditions. Recent conclusions of a European thematic workgroup demonstrate that this parameter is important to foresee the possible contamination of food by substances from packaging for regulation purpose [6]. In general, the migration and diffusion coefficients can be experimentally obtained from the migration test. Based on the type of additive, analytical techniques like gas chromatography, liquid chromatography, nuclear magnetic resonance spectroscopy, proton-induced X-ray emission, proton-induced gamma-ray emission and infrared spectroscopy have been widely used the migration test [7–9]. However, when the additive molecules are immersed in polymer matrix, direct measurement of the migration and diffusion coefficient is difficult and expensive due to the long experiment time and specific experimental procedures [10]. European Commission introduces diffusion modeling as an alternative to predict the migration and diffusion coefficient for both compliance testing and risk assessment. The currently general accepted model for the prediction of diffusion coefficients in packaging

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polymers is Piringer model [6]. Although empirical equation offers an interesting alternative, there are many limitations in this predictive approach for risk assessment. First, the availability of physicochemical properties for a wide range of additives and polymers under particular thermodynamic conditions is relative rare. Second, most mathematical modeling consider only the effect of additive and polymer material, ignore the effect of food on migration. Thus, a more precise prediction of the diffusion coefficients of migrant from polymer to food or food simulant is necessary for consumer exposure evaluation.

With the ever-growing computational power and the development of theoretical models, computer simulation technique provides a new way to study the migration process. The modeling of time evolution of the polymer and diffusant system at atomic scale has been applied for small weighted molecules (water and gases) in pure polymers [11,12], polymer blends [13,14], organic-inorganic hybrid members [15] and nanomaterials [16]. In our previous work, molecular dynamics (MD) simulation has been successfully used to investigate the diffusion behavior of small molecules and additives in polypropylene (PP) [17,18] and polyethylene terephthalate (PET) [19,20]. It should be noted that all of these dynamics simulation works were performed on polymer phase, and the diffusion coefficient obtained is only valid in polymer. In fact, the migration of additive from polymer material to food involves the diffusion between two phase substances, and is significantly influenced by food. In this context, the current work examines an approach based on two-phase MD simulation, at a reasonable computational cost, to simulate the migration of five additives [2,6-di-tert-butyl-4-methylphenol (BHT), 2-(2-Hydroxy-5-methylphenyl) benzotriazole (UV-P), 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV-327), 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (UV-329) and 2-hydroxy-4-(octyloxy) benzophenone (UV-531)] from PP material to food simulants. The overall goal is to understand the mechanisms of migration from a molecular point of view, and obtain some material's structural and dynamic details especially for the diffusion coefficients of additives in the migration process.

The present paper is organized as follows: Section 2 details the force field used and computational procedure; Section 3 describes the experimental investigation; Section 4 is devoted to the results and discussion; and finally, Section 5 summarizes the main findings and sketches the future work.

2. Molecule dynamics simulation

Fig. 1 presents the migration process of additives from polymer packaging to food. Additives are initially well dispersed in packaging and absented in food. With the increasing of time, additive molecules migrate into food gradually. In fact, food molecules are also able to migrate into polymer. This means the mass transfer is bidirectional. However, more attention is paid to the migration of additives for consumer safety and health. In this work, two-phase MD model is developed to investigate the migration process.

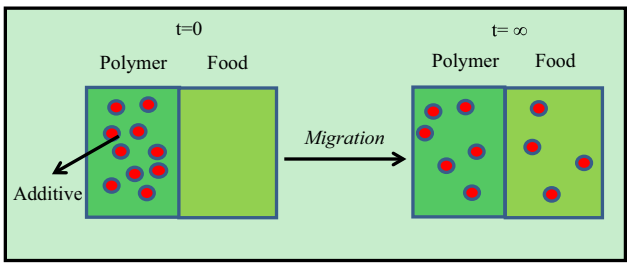

Fig. 1. Migration process of additives from polymer packaging to food.

The construction and equilibration of MD models, execution of long MD simulations and a detailed analysis of the atomistic configurations gathered are performed based on Materials Studio 7.0 platform of Accelrys, Inc. (San Diego, CA, USA).

2.1. Principle of MD simulation

MD simulation is a method based on classical mechanics. The atoms in system are simulated as particles, each particle has its own coordinate, mass, charge and chemical bonding. The initial position and velocity of particle are set according to Boltzmann random distribution. On the basis of force field potential, the force and interaction energies between particles are calculated. Then the velocity and acceleration of every atom are calculated by solving the Newton motion equation. At this moment, the new coordinate of atom is confirmed. Repeat this process until to complete the set simulation steps, and the coordinate and velocity of atoms at different time are output to obtain the trajectories of phase space. According to the motion trajectories, the corresponding physical characteristics are obtained by statistical physics and thermodynamic principles.

2.2. Force filed

A condensed-phase optimized molecular potentials for atomistic simulation studies II (COMPASS II) force field that derived from *ab initio* calculation has been successfully used in previous investigations of organic and inorganic materials [21–23]. This force field is also applied here to simulate the interactions among polymer, additive and food simulant molecules. The force field potential can be represented as [24]:

$$E_{total} = E_{valence} + E_{cross-term} + E_{nonbond} \tag{1}$$

where $E_{valence}$ is the valence energy, including bond stretching, bond angle blending, dihedral angle torsion and inversion potentials; $E_{cross-term}$ is the cross-term interacting energy. The cross terms is related to stretch-stretch, stretch-bend-stretch, bend-bend, torsion-stretch, torsion-bend-bend, bend-torsion-bend and stretch-torsion-stretch; $E_{nonbond}$ is the non-bond interacting energy. Each term is detailed as follows:

$$\begin{aligned} E_{valence} = & \sum_{b}[K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4] \\ & + \sum_{\theta}[H_2(\theta-\theta_0)^2 + H_3(\theta-\theta_0)^3 + H_4(\theta-\theta_0)^4] \\ & + \sum_{\phi}\{V_1[1-\cos(\phi-\phi_1^0)] + V_2[1-\cos(2\phi-\phi_2^0)] \\ & + V_3[1-\cos(3\phi-\phi_3^0)]\} + \sum_{\chi}K_\chi\chi^2 \end{aligned} \tag{2}$$

$$\begin{aligned} E_{cross-term} = & \sum_{b}\sum_{b'}K_{bb'}(b-b_0)(b'-b_0') + \sum_{\theta}\sum_{\theta'}K_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta_0') \\ & + \sum_{b}\sum_{\theta}K_{b\theta}(b-b_0)(\theta-\theta_0) \\ & + \sum_{b}\sum_{\phi}F_{b\phi}(b-b_0)(V_1\cos\phi + V_2\cos 2\phi + V_3\cos 3\phi) \\ & + \sum_{b'}\sum_{\phi}F_{b'\phi}(b'-b_0')(V_1\cos\phi + V_2\cos 2\phi + V_3\cos 3\phi) \\ & + \sum_{\theta}\sum_{\phi}F_{\theta\phi}(\theta-\theta_0)(V_1\cos\phi + V_2\cos 2\phi + V_3\cos 3\phi) \\ & + \sum_{\phi}\sum_{\theta}\sum_{\theta'}K_{\phi\theta\theta'}\cos\phi(\theta-\theta_0)(\theta'-\theta_0') \end{aligned} \tag{3}$$

$$E_{nonbond} = \sum_{ij}D_0\left[2\left(\frac{r_{m,ij}}{r_{ij}}\right)^9 - 3\left(\frac{r_{m,ij}}{r_{ij}}\right)^6\right] + \sum_{ij}C\frac{q_iq_j}{\varepsilon r_{ij}} \tag{4}$$